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Quantum-Chemical Calculation of Steric Structure of the Complexes Formed at Template Synthesis in Three-Component Systems of Co(II) [Ni(II), Cu(II)] Ion–Bithiooxamide–Acetone

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Abstract—By means of hybrid method of the density functional B3LYP with 6-31G(d) basis set we carried out calculation of geometric parameters of Co(II), Co(III), Ni(II) and Cu(II) complexes with macrocyclic ligand formed at the template processes in the systems M(II)–dithiooxamide–acetone with NNSS-coordination of donor centers. Atomic coordinates, bond lengths, bond angles and dihedral angles in the complexes with metallochelate node MN_2S_2 are listed. In the cases of Ni(II) and Cu(II) this chelate node is practically planar while in the case of Co(II) is tetrahedral. An additional six-membered metallocycle formed as a result of template "stitching" is screwed and turned by enough significant angle relative to five-membered rings.

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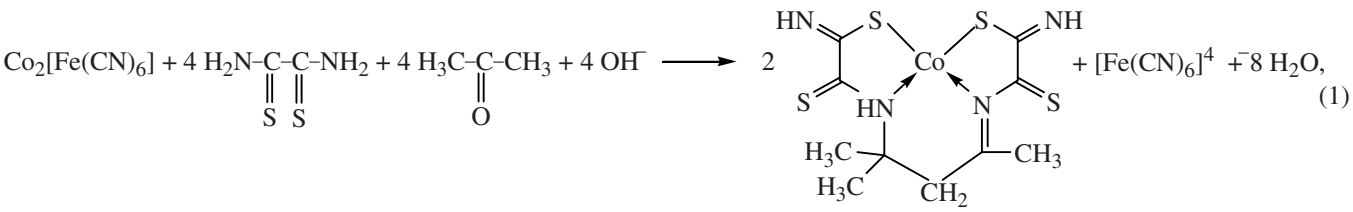
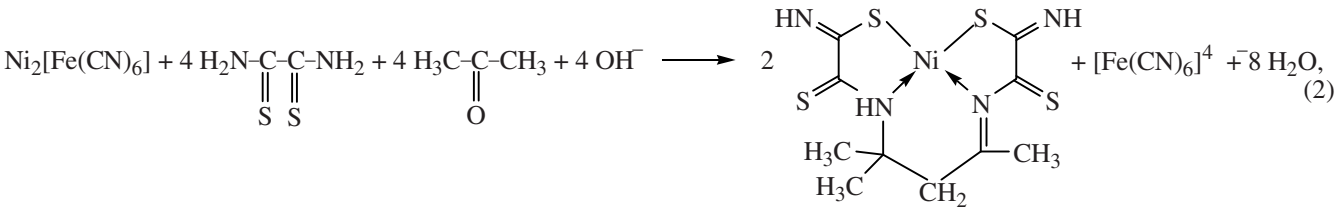
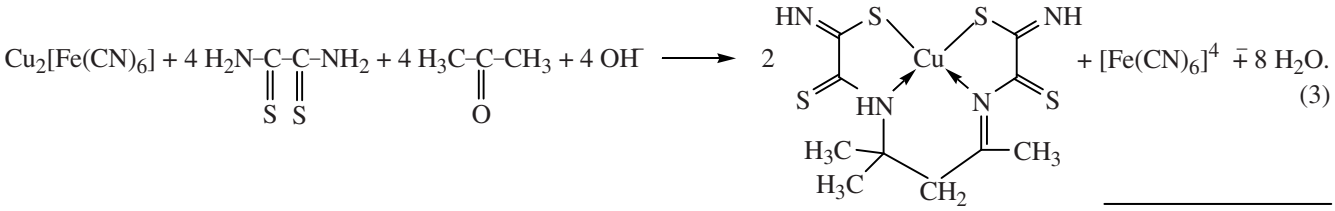
Earlier has been shown experimentally that for three-component systems Co(II) ion–dithiooxamide–acetone, Ni(II) ion–dithiooxamide–acetone and Cu(II) ion–dithiooxamide–acetone at the complex formation in respective metal-hexacyanoferrate(II) gelatin-immobilized matrices proceeds a template synthesis [1–5]. In each of the mentioned systems takes place inner sphere transformation of dithiooxamide and acetone resulting in formation one and same chelant 4,6,6-trimethyl-2,8-dithio-3,7-diazanonene-4-dithioamide-1,9 coordinating Co(II), Ni(II) and Cu(II) by two N and two S atoms (NNSS-coordination). Such coordination of 4,6,6-trimethyl-2,8-dithio-3,7-diazanonene-4-dithioamide-1,9 with these complex forming agents is in line with the concept of hard–soft acids and bases [6,7]. Exact steric structure of "template" complexes formed in such systems has not been established so far because despite efforts the monocrystals appropriate for X-ray structural analysis have not been successfully prepared [1–5]. This is why seems actual to perform nonempirical quantum-chemical calculation using any modern and tested method allowing to obtain independent objective data on their structural and geometric parameters. This communication is denoted to presenting and discussing the results of nonempirical quantum-chemical calculation of structures of the metallocomplexes formed in such systems, by one of the most popular methods, namely, hybrid method of density functional B3LYP.

According to the data [1–5], the template processes in three-component systems Co(II)–dithiooxamide–acetone, Ni(II)–dithiooxamide–acetone and Cu(II)–dithiooxamide–acetone can be described by the general schemes (1), (2) and (3), respectively:

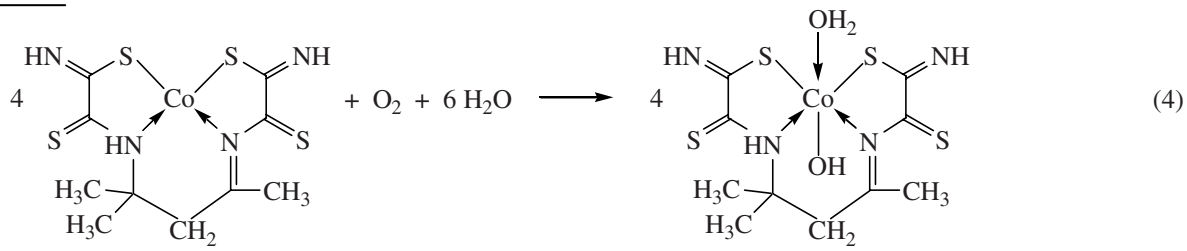






The complex of Co(II) further is oxidized to the complex of Co(III) with the same tetradentate ligand along the scheme (4).

The structures obtained in our quantum-chemical calculations of the complexes of Co(II), Ni(II), Cu(II) and Co(III) formed along the schemes (1)–(3) are depicted respectively in Figs. 1, 2, 3 and 4. The key data of these calculations, namely, Cartesian coordinates of all atoms, bond lengths, bond angles and dihedral angles are listed in Tables 1–4.



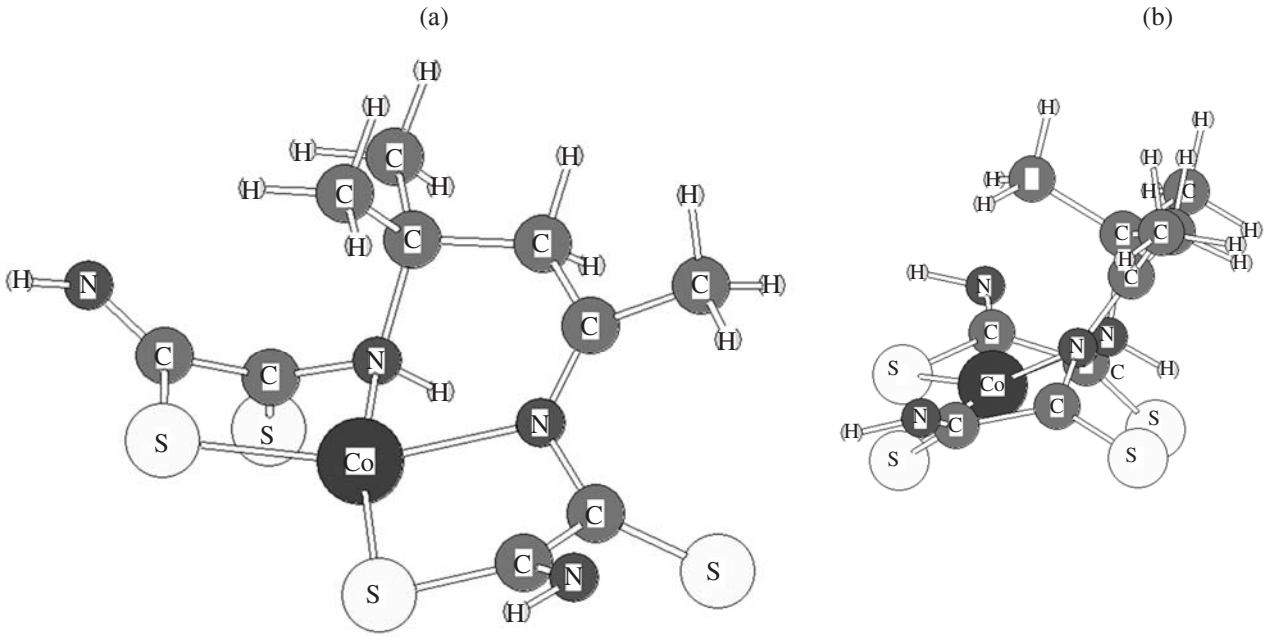


Fig. 1. Steric structure of "template" complex of Co(II) with 4,6,6-trimethyl-2,8-dithio-3,7-diazanonene-4-dithioamide-1,9: (a) front view, (b) side view.

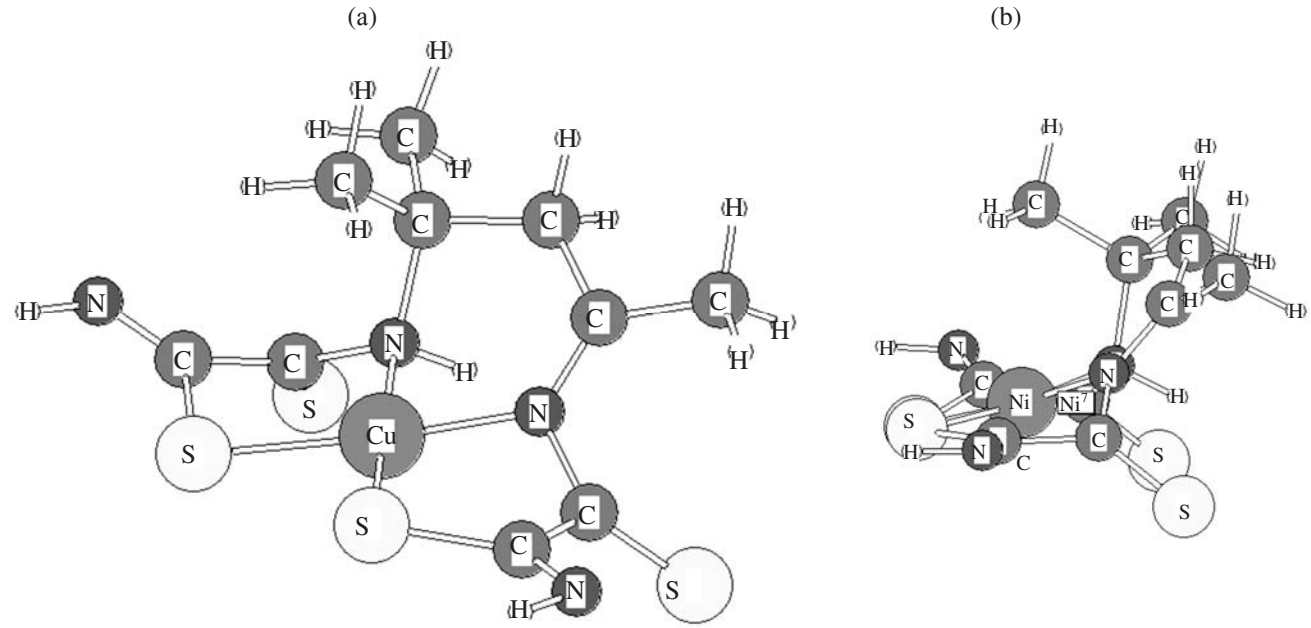


Fig. 2. Steric structure of "template" complex of Ni(II) with 4,6,6-trimethyl-2,8-dithio-3,7-diazanonene-4-dithioamide-1,9: (a) front view, (b) side view.

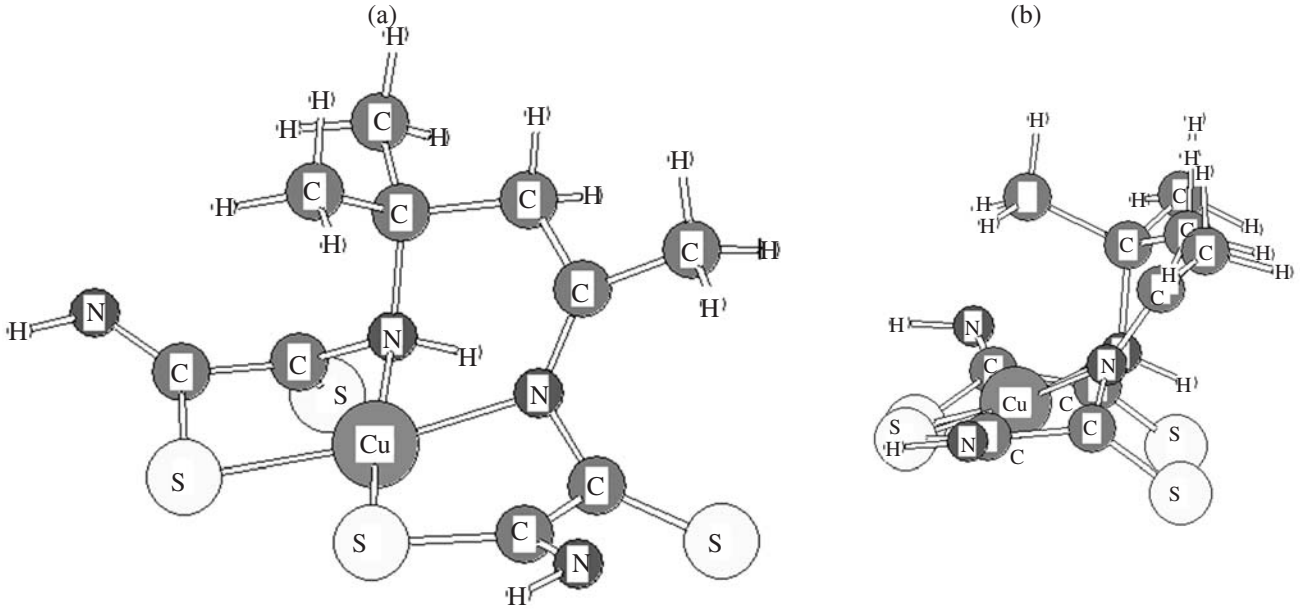
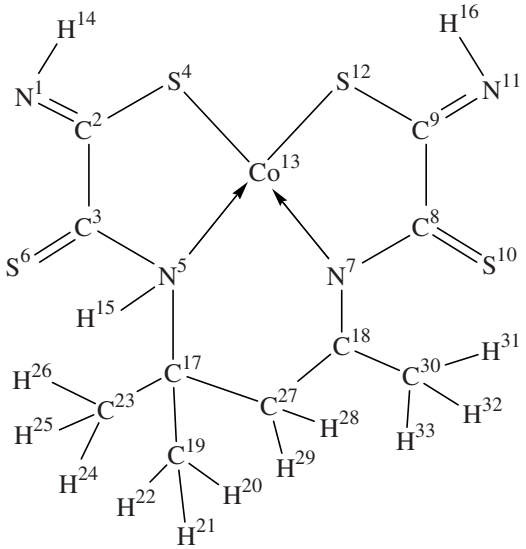


Fig. 3. Steric structure of "template" complex of Cu(II) with4,6,6-trimethyl-2,8-dithio-3,7-diazanonene-4-dithioamide-1,9: (a) front view, (b) side view.

Analysis of the data obtained shows that in the complexes of Ni(II) and Cu(II) with the above chelant the energetically most advantageous is coplanar orientation of the chelant donor centers relatively to the central metal ion, while for the complex of Co(II) the best one is tetrahedral orientation. As expected, the ground state of the cobalt complex is spin quadruplet, for nickel spin singlet and for copper complex spin doublet. Therewith, the quadruplet state of Co(II) complex energetically is preferable over doublet by 10.18 kJ mol^{-1}, singlet state of Ni(II) is preferable over triplet by 25.60 kJ mol^{-1} and, finally, doublet state of Cu(II) complex is advantageous over quadruplet by 93.9 kJ mol^{-1}. Average bond lengths of the bonds M–

N and M–S in the complexes with planar chelate node N_2S_2 are 187.7 and 219.9 pm for Ni(II), 203.0 and 227.5 pm for Cu(II) complexes. In the complex of Co(II) with tetrahedral chelate node N_2S_2 these bonds are longer than in the complexes of Ni(II) and Cu(II) (214.9 and 228.0 pm, respectively). As can be easily seen, they differ mutually significantly. It is significant that additional six-membered ring formed as a result of template "stitching" even in the cases of Ni(II) and Cu (II) complexes with planar chelate N_2S_2 node is not in the same plane with this node but is tilt to it. Moreover, this additional ring is very screwed and has no sets of four atoms in a plane. In the nickel complex the angle between atoms $Co^{13}N^5C^{18}$ is 107.6°, between $Co^{13}N^5,C^{17}$ 126.2°; the dihedral angle between the atoms $C^2C^3N^5C^{18}$ is 130.6°, between the atoms $C^2C^3N^5C^{17}$ is 69.0°. Related angles in copper(II) complex are 105.2°, 126.6°, 121.0°, and 73.5°, respectively. In this connection, it is noticeable that metallochelate nodes MN_2S_2 in both Ni(II) and Cu(II) complexes are practically planar. This conclusion obeys completely to experimental data [2–5] which

Table 1. Calculated structural geometric parameters of Co(II) complex



Atom no.	Element	Cartesian coordinates, pm			Atom no.	Element	Cartesian coordinates, pm		
		x	*y*	*z*			*x*	*y*	*z*
1	N	422.8614	95.7434	7.0284	18	C	–140.7454	–119.2689	147.6312
2	C	303.8411	82.0303	–36.8901	19	C	244.5745	–190.0153	196.6919
3	C	252.4201	–56.3321	–64.3440	20	H	239.7079	–209.5353	304.3496
4	S	183.7882	207.0527	–78.6813	21	H	244.3395	–286.1887	144.2311
5	N	128.4001	–86.8284	0.9747	22	H	339.3890	–139.6982	175.3762
6	S	319.1139	–159.7475	–171.7625	23	C	132.4874	32.6267	227.6240
7	N	–154.5414	–47.4276	40.9459	24	H	130.7176	12.3296	335.2614
8	C	–280.0476	–22.3382	–19.9470	25	H	224.3642	86.9520	205.4049
9	C	–304.7237	122.7573	–49.9917	26	H	47.6079	97.9450	205.1268
10	S	–378.0994	–143.3338	–70.6066	27	C	–5.4053	–174.8195	188.2688
11	N	–417.7729	171.6755	–17.2882	28	H	–2.8101	–276.2863	144.8964
12	S	–169.0302	203.2835	–133.1952	29	H	–5.7552	–190.5660	296.6035
13	Co	–3.0389	75.0438	–0.3660	30	C	–254.3006	–162.0718	236.9143
14	H	445.0420	195.2646	17.9840	31	H	–347.7103	–110.8897	214.0726
15	H	96.7040	–175.8002	–38.2262	32	H	–271.2358	–270.0352	227.3086
16	H	–422.4288	270.5733	–43.9410	33	H	–226.5718	–142.8528	341.2062
17	C	126.1825	–101.8372	153.4648					

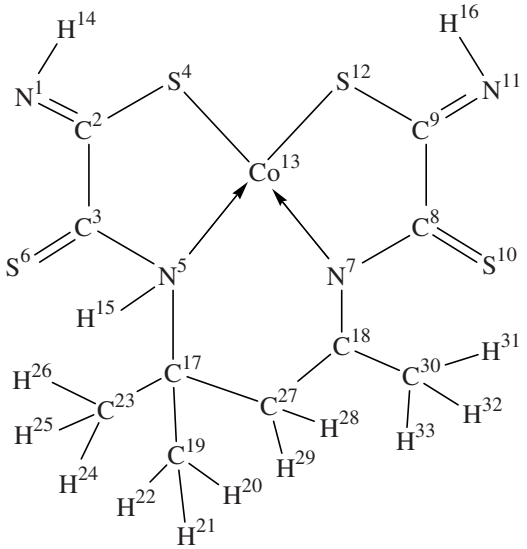
Table 1. (Contd.)

Bond lengths, pm		Bond lengths, pm		Bond lengths, pm		Bond lengths, pm	
d(1,2)	127.60	*d*(5,17)	153.24	*d*(12,13)	225.52	*d*(23,24)	109.55
d(1,14)	102.55	*d*(7,8)	141.74	*d*(17,19)	153.82	*d*(23,25)	109.02
d(2,3)	150.14	*d*(7,13)	215.15	*d*(17,23)	153.69	*d*(23,26)	109.44
d(2,4)	178.30	*d*(7,18)	129.36	*d*(17,27)	154.44	*d*(27,28)	110.38
d(3,5)	143.45	*d*(8,9)	150.21	*d*(18,27)	151.84	*d*(27,29)	109.47
d(3,6)	163.34	*d*(8,10)	163.77	*d*(18,30)	150.66	*d*(30,31)	108.93
d(4,13)	230.50	*d*(9,11)	127.45	*d*(19,20)	109.52	*d*(30,32)	109.70
d(5,13)	214.74	*d*(9,12)	178.38	*d*(19,21)	109.55	*d*(30,33)	109.61
d(5,15)	102.26	*d*(11,16)	102.53	*d*(19,22)	109.43		
Bond angles, deg		Dihedral angles, deg		Bond angles, deg		Dihedral angles, deg	
A(2,1,14)	110.0478	D(4,13,7,12)	195.0344	A(7,18,27)	121.2642	D(8,9,11,16)	–179.3599
A(1,2,3)	118.7782	D(5,13,12,7)	192.4746	A(7,18,30)	124.4820	D(12,9,11,16)	–1.3564
A(1,2,4)	129.2981	D(14,1,2,3)	178.0806	A(27,18,30)	114.1598	D(8,9,12,13)	–28.4698
A(3,2,4)	111.8842	D(14,1,2,4)	0.5691	A(17,19,20)	110.1338	D(11,9,12,13)	153.4626
A(2,3,5)	114.1267	D(1,2,3,5)	126.4942	A(17,19,21)	111.5324	D(9,12,13,4)	–159.1782
A(2,3,6)	124.3231	D(1,2,3,6)	–60.3668	A(17,19,22)	110.3978	D(9,12,13,7)	5.7874
A(5,3,6)	121.1880	D(4,2,3,5)	–55.5809	A(20,19,21)	108.3101	D(5,17,19,20)	–174.8897
A(2,4,13)	96.6253	D(4,2,3,6)	117.5580	A(20,19,22)	108.1746	D(5,17,19,21)	–54.6005
A(3,5,13)	105.0736	D(1,2,4,13)	–155.9907	A(21,19,22)	108.1935	D(5,17,19,22)	65.7193
A(3,5,15)	106.1639	D(3,2,4,13)	26.3598	A(17,23,24)	108.1404	D(23,17,19,20)	60.8019
A(3,5,17)	119.1069	D(2,3,5,13)	51.5802	A(17,23,25)	111.8508	D(23,17,19,21)	–178.9089
A(13,5,15)	111.9917	D(2,3,5,15)	170.3859	A(17,23,26)	113.0277	D(23,17,19,22)	–58.5891
A(13,5,17)	107.6303	D(2,3,5,17)	–69.0139	A(24,23,25)	107.8292	D(27,17,19,20)	–59.2706
A(15,5,17)	106.9633	D(6,3,5,13)	–121.7972	A(24,23,26)	107.4595	D(27,17,19,21)	61.0186
A(8,7,13)	109.9034	D(6,3,5,15)	–2.9915	A(25,23,26)	108.3188	D(27,17,19,22)	–178.6616
A(8,7,18)	123.1662	D(6,3,5,17)	117.6087	A(17,27,18)	121.7520	D(5,17,23,24)	–179.8346
A(13,7,18)	126.2323	D(2,4,13,5)	–0.3995	A(17,27,28)	109.0149	D(5,17,23,25)	–61.2462
A(7,8,9)	113.7267	D(2,4,13,12)	–170.4886	A(17,27,29)	107.0795	D(5,17,23,26)	61.3284
A(7,8,10)	122.1592	D(3,5,13,4)	–25.7309	A(18,27,28)	104.6024	D(19,17,23,24)	–58.0446
A(9,8,10)	123.6017	D(3,5,13,7)	170.9940	A(18,27,29)	108.3386	D(19,17,23,25)	60.5439
A(8,9,11)	117.7196	D(15,5,13,4)	–140.5466	A(28,27,29)	104.8746	D(19,17,23,26)	–176.8815
A(8,9,12)	113.8520	D(15,5,13,7)	56.1783	A(18,30,31)	112.8648	D(27,17,23,24)	61.3540
A(11,9,12)	128.4021	D(17,5,13,4)	102.1625	A(18,30,32)	110.1242	D(27,17,23,25)	179.9424
A(9,11,16)	110.1088	D(17,5,13,7)	–61.1126	A(18,30,33)	108.8665	D(27,17,23,26)	–57.4830
A(9,12,13)	97.5786	D(3,5,17,19)	–46.0515	A(31,30,32)	108.1590	D(5,17,27,18)	–57.5097
A(4,13,5)	87.9924	D(3,5,17,23)	76.0687	A(31,30,33)	109.5142	D(5,17,27,28)	64.2843
A(4,13,12)	103.0496	D(3,5,17,27)	–163.1591	A(32,30,33)	107.1522	D(5,17,27,29)	177.2345
A(5,13,7)	84.2868	D(13,5,17,19)	–165.3431			D(19,17,27,18)	–174.7420
A(7,13,12)	87.7805	D(13,5,17,23)	–43.2229			D(19,17,27,28)	–52.9480
A(5,17,19)	108.9444	D(13,5,17,27)	77.5493			D(19,17,27,29)	60.0022
A(5,17,23)	113.1960	D(15,5,17,19)	74.1435			D(23,17,27,18)	65.3850
A(5,17,27)	106.4306	D(15,5,17,23)	–163.7363			D(23,17,27,28)	–172.8210
A(19,17,23)	109.5343	D(15,5,17,27)	–42.9641			D(23,17,27,29)	–59.8708
A(19,17,27)	108.7569	D(13,7,8,9)	–40.3482			D(7,18,27,17)	29.8314
A(23,17,27)	109.8558	D(13,7,8,10)	131.7135			D(7,18,27,28)	–94.0295

Table 1. (Contd.)

Dihedral angles, deg		Dihedral angles, deg	
D(7,18,27,29)	154.5123	D(7,18,30,32)	109.8721
D(30,18,27,17)	–153.5421	D(7,18,30,33)	–132.9254
D(30,18,27,28)	82.5970	D(27,18,30,31)	172.3902
D(30,18,27,29)	–28.8612	D(27,18,30,32)	–66.6294
D(7,18,30,31)	–11.1082	D(27,18,30,33)	50.5730

Table 2. Calculated structural geometric parameters of Ni(II) complex



Atom no.	Element	Cartesian coordinates, pm			Atom no.	Element	Cartesian coordinates, pm		
		x	*y*	*z*			*x*	*y*	*z*
1	C	406.5559	–122.0368	–53.4832	18	C	–135.3475	182.3623	–46.1125
2	C	286.8945	–111.4291	–10.4782	19	C	248.0521	251.4247	–83.5452
3	C	247.4687	5.3271	73.6304	20	H	242.5990	326.5760	–163.0368
4	S	149.2835	–222.4106	–25.0110	21	H	253.1431	303.5617	12.6438
5	N	122.7445	65.9964	31.0304	22	H	340.7577	194.8161	–96.6406
6	S	321.9299	53.0060	210.4735	23	C	129.7868	79.9582	–223.6461
7	N	–143.0784	61.1335	–1.7382	24	H	141.3083	151.4434	–305.9006
8	C	–262.6204	5.7923	54.3483	25	H	214.7460	11.5289	–227.0499
9	C	–303.1149	–119.6572	–16.9629	26	H	38.4455	22.6070	–241.1279
10	S	–332.7687	66.2335	188.7614	27	C	–2.3512	244.5046	–83.2860
11	N	–427.4155	–143.0772	–33.4413	28	H	13.0198	325.2949	–9.7651
12	S	–162.4046	–215.7526	–65.7140	29	H	–14.2681	296.2355	–179.2425
13	Ni	–9.4727	–70.6516	–5.1363	30	C	–253.6159	274.9052	–58.1489
14	H	417.5959	–208.9623	–106.7654	31	H	–347.6727	220.5484	–68.4111
15	H	93.8873	124.6369	109.8444	32	H	–261.5167	338.0414	31.1903
16	H	–440.9216	–231.2330	–84.0031	33	H	–240.3524	340.8312	–144.4872
17	C	125.8774	158.6433	–91.8264					

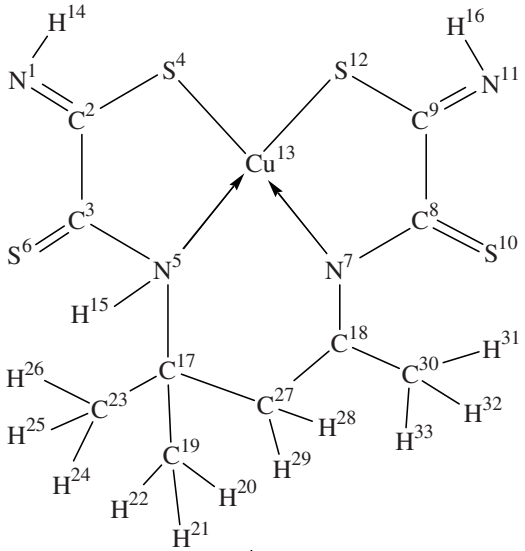
Table 2. (Contd.)

Bond lengths, pm		Bond lengths, pm		Bond lengths, pm		Bond lengths, pm	
d(1,2)	127.60	*d*(7,8)	143.17	*d*(17,19)	153.63	*d*(23,25)	109.14
d(1,14)	102.55	*d*(7,13)	187.69	*d*(17,23)	153.57	*d*(23,26)	109.26
d(2,3)	149.20	*d*(7,18)	129.33	*d*(17,27)	154.56	*d*(27,28)	110.31
d(2,4)	177.38	*d*(8,9)	149.88	*d*(18,27)	151.43	*d*(27,29)	109.66
d(3,5)	145.09	*d*(8,10)	163.22	*d*(18,30)	150.65	*d*(30,31)	109.12
d(3,6)	162.92	*d*(9,11)	127.56	*d*(19,20)	109.53	*d*(30,32)	109.68
d(4,13)	220.52	*d*(9,12)	177.23	*d*(19,21)	109.53	*d*(30,33)	109.44
d(5,15)	102.39	*d*(11,16)	102.52	*d*(19,22)	109.41		
d(5,17)	153.91	*d*(12,13)	219.34	*d*(23,24)	109.58		
Bond angles, deg		Dihedral angles, deg		Bond angles, deg		Dihedral angles, deg	
A(2,1,14)	110.2757	D(4,13,7,12)	184.2210	A(17,19,21)	111.8247	D(8,9,11,16)	179.5548
A(1,2,3)	120.1901	D(14,1,2,3)	178.1561	A(17,19,22)	110.7876	D(12,9,11,16)	–0.8914
A(1,2,4)	130.3843	D(14,1,2,4)	2.3776	A(20,19,21)	108.2448	D(8,9,12,13)	–5.8750
A(3,2,4)	109.3170	D(1,2,3,5)	133.3281	A(20,19,22)	108.0790	D(11,9,12,13)	174.5468
A(2,3,5)	112.8833	D(1,2,3,6)	–53.9510	A(21,19,22)	108.1810	D(9,12,13,4)	166.9188
A(2,3,6)	125.5725	D(4,2,3,5)	–50.0782	A(17,23,24)	108.2244	D(9,12,13,7)	–17.3022
A(5,3,6)	121.1390	D(4,2,3,6)	122.6427	A(17,23,25)	111.5820	D(5,17,19,20)	–172.0014
A(2,4,13)	96.9235	D(1,2,4,13)	–154.8779	A(17,23,26)	112.6442	D(5,17,19,21)	–51.9539
A(3,5,15)	104.8184	D(3,2,4,13)	28.9881	A(24,23,25)	107.6824	D(5,17,19,22)	68.8126
A(3,5,17)	117.9426	D(2,3,5,15)	164.2355	A(24,23,26)	108.0717	D(23,17,19,20)	64.4490
A(15,5,17)	105.9882	D(2,3,5,17)	–78.1938	A(25,23,26)	108.4614	D(23,17,19,21)	–175.5034
A(8,7,13)	109.2707	D(6,3,5,15)	–8.8490	A(17,27,18)	120.9471	D(23,17,19,22)	–54.7369
A(8,7,18)	123.1379	D(6,3,5,17)	108.7217	A(17,27,28)	109.1527	D(27,17,19,20)	–56.6640
A(13,7,18)	127.5460	D(2,4,13,12)	169.1645	A(17,27,29)	107.6901	D(27,17,19,21)	63.3835
A(7,8,9)	111.2685	D(3,5,17,19)	–43.3719	A(18,27,28)	105.0293	D(27,17,19,22)	–175.8500
A(7,8,10)	122.5684	D(3,5,17,23)	78.6579	A(18,27,29)	108.2366	D(5,17,23,24)	–174.7913
A(9,8,10)	125.8497	D(3,5,17,27)	–160.5253	A(28,27,29)	104.6457	D(5,17,23,25)	–56.4884
A(8,9,11)	118.5835	D(15,5,17,19)	73.5731	A(18,30,31)	112.2219	D(5,17,23,26)	65.7878
A(8,9,12)	111.7284	D(15,5,17,23)	–164.3970	A(18,30,32)	110.1860	D(19,17,23,24)	–52.7185
A(11,9,12)	129.6868	D(15,5,17,27)	–43.5803	A(18,30,33)	109.7510	D(19,17,23,25)	65.5845
A(9,11,16)	110.4855	D(13,7,8,9)	–53.4638	A(31,30,32)	107.5335	D(19,17,23,26)	–172.1394
A(9,12,13)	96.8288	D(13,7,8,10)	120.4511	A(31,30,33)	109.2908	D(27,17,23,24)	67.2145
A(4,13,12)	91.2492	D(18,7,8,9)	124.2541	A(32,30,33)	107.7325	D(27,17,23,25)	–174.4825
A(7,13,12)	88.4626	D(18,7,8,10)	–61.8310			D(27,17,23,26)	–52.2064
A(5,17,19)	109.6757	D(8,7,13,12)	40.1946			D(5,17,27,18)	–43.1904
A(5,17,23)	112.1659	D(18,7,13,12)	–137.3951			D(5,17,27,28)	78.7017
A(5,17,27)	105.8677	D(8,7,18,27)	169.7193			D(5,17,27,29)	–168.2370
A(19,17,23)	109.6002	D(8,7,18,30)	–6.8711			D(19,17,27,18)	–160.9701
A(19,17,27)	108.7413	D(13,7,18,27)	–12.9980			D(19,17,27,28)	–39.0780
A(23,17,27)	110.6830	D(13,7,18,30)	170.4116			D(19,17,27,29)	73.9834
A(7,18,27)	121.4263	D(7,8,9,11)	–143.8120			D(23,17,27,18)	78.5835
A(7,18,30)	123.8003	D(7,8,9,12)	36.5577			D(23,17,27,28)	–159.5243
A(27,18,30)	114.6942	D(10,8,9,11)	42.5158			D(23,17,27,29)	–46.4630
A(17,19,20)	109.6122	D(10,8,9,12)	–137.1145			D(7,18,27,17)	10.1763

Table 2. (Contd.)

Dihedral angles, deg		Dihedral angles, deg	
D(7,18,27,28)	–113.6782	D(7,18,30,32)	94.6951
D(7,18,27,29)	134.9690	D(7,18,30,33)	–146.8285
D(30,18,27,17)	–172.9419	D(27,18,30,31)	158.1001
D(30,18,27,28)	63.2036	D(27,18,30,32)	–82.1028
D(30,18,27,29)	–48.1492	D(27,18,30,33)	36.3736
D(7,18,30,31)	–25.1021		

Table 3. Calculated structural geometric parameters of Cu(II) complex



Atom no.	Element	Cartesian coordinates, pm			Atom no.	Element	Cartesian coordinates, pm		
		x	*y*	*z*			*x*	*y*	*z*
1	N	419.2641	91.9287	–12.4585	18	C	–142.0420	–120.9029	140.9608
2	C	299.6781	73.3677	–53.1379	19	C	242.1437	–181.6716	201.6694
3	C	247.3682	–66.2930	–66.2209	20	H	236.6571	–197.9465	309.8391
4	S	178.0653	191.0145	–107.2094	21	H	243.8324	–279.3746	152.1890
5	N	122.8402	–87.8446	2.3345	22	H	336.3593	–130.5706	179.5528
6	S	311.6676	–181.2360	–162.6010	23	C	128.5135	41.5377	222.0357
7	N	–150.0711	–46.0789	36.1435	24	H	136.1086	27.1684	330.3646
8	C	–272.6756	–16.4115	–29.2962	25	H	215.9890	98.2424	189.8712
9	C	–300.9136	131.0457	–34.3400	26	H	39.1204	101.7433	203.1953
10	S	–361.1091	–131.9757	–103.5348	27	C	–8.1673	–169.1710	193.5259
11	N	–422.0332	168.2043	–18.3643	28	H	–1.3316	–274.9691	162.9530
12	S	–157.2322	231.3854	–62.7842	29	H	–13.3451	–171.9171	302.9159
13	Cu	–2.7308	67.0525	–42.2934	30	C	–261.8160	–172.9319	216.2395
14	H	441.2241	192.0884	–11.7696	31	H	–352.5408	–116.6268	194.0650
15	H	86.8511	–176.8902	–32.7622	32	H	–280.0881	–277.7679	189.4970
16	H	–428.7462	270.4007	–23.1459	33	H	–242.1917	–169.4327	323.8791
17	C	122.7493	–96.7606	155.2885					

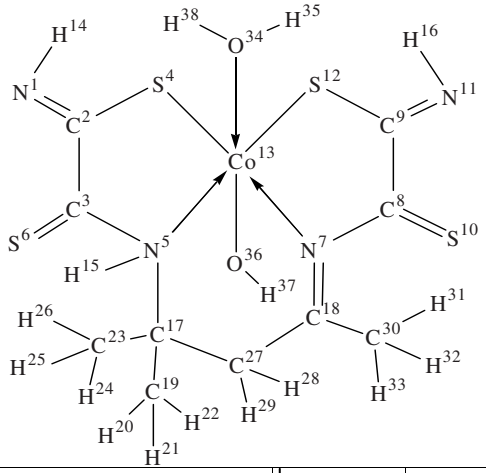
Table 3. (Contd.)

Bond lengths, pm		Bond lengths, pm		Bond lengths, pm		Bond lengths, pm	
d(1,2)	127.67	*d*(5,17)	153.21	*d*(12,13)	226.49	*d*(23,24)	109.54
d(1,14)	102.54	*d*(7,8)	142.11	*d*(17,19)	153.68	*d*(23,25)	109.10
d(2,3)	149.71	*d*(7,13)	201.64	*d*(17,23)	153.67	*d*(23,26)	109.41
d(2,4)	177.63	*d*(7,18)	129.03	*d*(17,27)	154.42	*d*(27,28)	110.34
d(3,5)	143.78	*d*(8,9)	150.22	*d*(18,27)	151.71	*d*(27,29)	109.55
d(3,6)	163.20	*d*(8,10)	163.36	*d*(18,30)	150.73	*d*(30,31)	109.05
d(4,13)	228.62	*d*(9,11)	127.69	*d*(19,20)	109.52	*d*(30,32)	109.73
d(5,13)	204.34	*d*(9,12)	177.54	*d*(19,21)	109.53	*d*(30,33)	109.47
d(5,15)	102.26	*d*(11,16)	102.53	*d*(19,22)	109.44		
Bond angles, deg		**Dihedral angles, deg**		**Bond angles, deg**		**Dihedral angles, deg**	
A(2,1,14)	110.1659	D(4,13,7,12)	185.9978	A(7,18,27)	121.3904	D(18,7,8,10)	–65.2129
A(1,2,3)	119.3899	D(5,13,12,7)	174.7971	A(7,18,30)	123.8080	D(8,7,13,5)	–149.3697
A(1,2,4)	129.9386	D(14,1,2,3)	178.1352	A(27,18,30)	114.7302	D(8,7,13,12)	35.8332
A(3,2,4)	110.6115	D(14,1,2,4)	1.2413	A(17,19,20)	109.9538	D(18,7,13,5)	39.4740
A(2,3,5)	113.6283	D(1,2,3,5)	127.3639	A(17,19,21)	111.6234	D(18,7,13,12)	–135.3231
A(2,3,6)	124.8179	D(1,2,3,6)	–59.9054	A(17,19,22)	110.4787	D(8,7,18,27)	169.4210
A(5,3,6)	121.1482	D(4,2,3,5)	–55.1801	A(20,19,21)	108.3235	D(8,7,18,30)	–7.3434
A(2,4,13)	95.5012	D(4,2,3,6)	117.5506	A(20,19,22)	108.1858	D(13,7,18,27)	–20.5611
A(3,5,13)	108.3302	D(1,2,4,13)	–151.0038	A(21,19,22)	108.1764	D(13,7,18,30)	162.6745
A(3,5,15)	105.7661	D(3,2,4,13)	31.8875	A(17,23,24)	108.3058	D(7,8,9,11)	–141.8906
A(3,5,17)	119.0288	D(2,3,5,13)	46.4302	A(17,23,25)	111.7027	D(7,8,9,12)	38.2380
A(13,5,15)	111.6463	D(2,3,5,15)	166.2532	A(17,23,26)	112.9408	D(10,8,9,11)	44.6084
A(13,5,17)	105.1760	D(2,3,5,17)	–73.5210	A(24,23,25)	107.7071	D(10,8,9,12)	–135.2630
A(15,5,17)	106.9634	D(6,3,5,13)	–126.5980	A(24,23,26)	107.4050	D(8,9,11,16)	179.6125
A(8,7,13)	109.5216	D(6,3,5,15)	–6.7750	A(25,23,26)	108.5624	D(12,9,11,16)	–0.5376
A(8,7,18)	123.2859	D(6,3,5,17)	113.4507	A(17,27,18)	120.8744	D(8,9,12,13)	–8.5259
A(13,7,18)	126.5736	D(2,4,13,5)	–6.9385	A(17,27,28)	109.1775	D(11,9,12,13)	171.6201
A(7,8,9)	112.4928	D(2,4,13,12)	167.1929	A(17,27,29)	107.4035	D(9,12,13,4)	172.6625
A(7,8,10)	121.9129	D(3,5,13,4)	–18.9869	A(18,27,28)	105.2917	D(9,12,13,7)	–13.3353
A(9,8,10)	125.2666	D(3,5,13,7)	166.6051	A(18,27,29)	108.1954	D(5,17,19,20)	–173.7133
A(8,9,11)	117.3702	D(15,5,13,4)	–135.0547	A(28,27,29)	104.8078	D(5,17,19,21)	–53.4685
A(8,9,12)	114.0801	D(15,5,13,7)	50.5373	A(18,30,31)	112.4139	D(5,17,19,22)	66.9448
A(11,9,12)	128.5496	D(17,5,13,4)	109.2944	A(18,30,32)	109.9014	D(23,17,19,20)	62.5186
A(9,11,16)	110.2625	D(17,5,13,7)	–65.1136	A(18,30,33)	109.7303	D(23,17,19,21)	–177.2366
A(9,12,13)	97.3253	D(3,5,17,19)	–42.5102	A(31,30,32)	107.7703	D(23,17,19,22)	–56.8233
A(4,13,5)	89.2588	D(3,5,17,23)	79.6470	A(31,30,33)	109.4246	D(27,17,19,20)	–58.2670
A(4,13,12)	96.9127	D(3,5,17,27)	–159.8547	A(32,30,33)	107.4601	D(27,17,19,21)	61.9778
A(5,13,7)	86.4900	D(13,5,17,19)	–164.0578			D(27,17,19,22)	–177.6089
A(7,13,12)	86.7793	D(13,5,17,23)	–41.9005			D(5,17,23,24)	–175.5983
A(5,17,19)	109.4506	D(13,5,17,27)	78.5977			D(5,17,23,25)	–57.1428
A(5,17,23)	112.4093	D(15,5,17,19)	77.1046			D(5,17,23,26)	65.5754
A(5,17,27)	105.9618	D(15,5,17,23)	–160.7381			D(19,17,23,24)	–53.5802
A(19,17,23)	109.6958	D(15,5,17,27)	–40.2399			D(19,17,23,25)	64.8754
A(19,17,27)	108.9567	D(13,7,8,9)	–50.4692			D(19,17,23,26)	–172.4064
A(23,17,27)	110.2589					D(27,17,23,24)	66.4144

Table 3. (Contd.)

Dihedral angles, deg		Dihedral angles, deg	
D(27,17,23,25)	–175.1301	D(7,18,27,28)	–103.8722
D(27,17,23,26)	–52.4119	D(7,18,27,29)	144.4879
D(5,17,27,18)	–52.2670	D(30,18,27,17)	–162.7590
D(5,17,27,28)	69.9597	D(30,18,27,28)	73.1681
D(5,17,27,29)	–176.9245	D(30,18,27,29)	–38.4718
D(19,17,27,18)	–169.9418	D(7,18,30,31)	–18.4888
D(19,17,27,28)	–47.7151	D(7,18,30,32)	101.5396
D(19,17,27,29)	65.4007	D(7,18,30,33)	–140.5015
D(23,17,27,18)	69.6186	D(27,18,30,31)	164.5519
D(23,17,27,28)	–168.1547	D(27,18,30,32)	–75.4197
D(23,17,27,29)	–55.0389	D(27,18,30,33)	42.5392
D(7,18,27,17)	20.2007		

Table 4. Calculated structural geometric parameters of Co(III) complex



Atom no.	Element	Cartesian coordinates, pm			Atom no.	Element	Cartesian coordinates, pm		
		x	*y*	*z*			*x*	*y*	*z*
1	N	400.2714	–124.5753	–78.1579	20	H	186.2402	399.2818	–25.8294
2	C	285.3616	–116.4708	–24.5454	21	H	93.6522	327.5863	107.2523
3	C	250.2002	–1.9856	65.7024	22	H	266.2150	290.8551	89.1817
4	S	151.1438	–234.3826	–24.8314	23	C	247.5784	170.3156	–163.9255
5	N	125.8090	64.9609	31.1395	24	H	251.4568	259.8006	–227.0288
6	S	330.5382	30.3846	204.1002	25	H	346.4100	156.1912	–119.2130
7	N	–145.4995	69.9279	–11.9063	26	H	224.0753	84.0800	–226.5528
8	C	–267.5091	25.3656	44.4645	27	C	4.3302	217.8492	–130.8453
9	C	–314.8154	–101.5914	–21.5634	28	H	4.8376	323.2273	–160.2198
10	S	–337.4610	93.7522	175.4803	29	H	2.8065	156.3347	–221.7855
11	N	–439.0635	–113.1539	–47.4039	30	C	–235.7717	289.4412	–82.0109
12	S	–184.0773	–219.4328	–48.8058	31	H	–335.9972	249.8562	–65.9768
13	Co	–11.6989	–74.1771	–21.8073	32	H	–219.2885	371.5516	–11.0749
14	H	408.3350	–211.1169	–132.4811	33	H	–229.0177	331.9838	–182.7398
15	H	88.6180	99.4776	119.9571	34	O	–25.3433	–103.6692	182.8425
16	H	–457.9024	–202.6278	–93.7834	35	H	–109.6199	–150.7795	197.7538
17	C	138.9286	190.1287	–57.7439	36	O	9.0340	–45.4852	–201.4736
18	C	–127.5055	186.4063	–65.4452	37	H	3.8922	–131.2985	–246.3225
19	C	173.3980	308.6234	34.2265	38	H	43.5396	–172.1373	196.0355

Table 4. (Contd.)

Bond lengths, pm		Bond lengths, pm		Bond lengths, pm		Bond lengths, pm	
d(1,2)	127.06	*d*(7,8)	141.60	*d*(13,36)	183.12	*d*(23,24)	109.57
d(1,14)	102.50	*d*(7,13)	196.89	*d*(17,19)	153.91	*d*(23,25)	109.39
d(2,3)	149.96	*d*(7,18)	129.45	*d*(17,23)	153.21	*d*(23,26)	109.14
d(2,4)	178.66	*d*(8,9)	150.72	*d*(17,27)	155.66	*d*(26,36)	252.31
d(3,5)	145.43	*d*(8,10)	163.51	*d*(18,27)	150.49	*d*(27,28)	109.40
d(3,6)	163.27	*d*(9,11)	127.43	*d*(18,30)	150.37	*d*(27,29)	109.80
d(5,13)	202.66	*d*(9,12)	178.10	*d*(19,20)	109.50	*d*(30,31)	108.95
d(5,15)	102.29	*d*(11,16)	102.53	*d*(19,21)	109.78	*d*(30,32)	109.75
d(5,17)	154.08	*d*(13,34)	207.21	*d*(19,22)	109.32	*d*(30,33)	109.55
Bond angles, deg		Dihedral angles, deg		Bond angles, deg		Dihedral angles, deg	
A(2,1,14)	110.4040	D(34,13,36,5)	178.6302	A(17,19,22)	111.4331	D(18,7,13,36)	–47.3461
A(1,2,3)	120.9761	D(14,1,2,3)	177.1235	A(20,19,21)	107.8791	D(8,7,18,27)	–175.5863
A(1,2,4)	129.5427	D(14,1,2,4)	4.0442	A(20,19,22)	108.1013	D(8,7,18,30)	–3.2426
A(3,2,4)	109.1887	D(1,2,3,5)	128.9774	A(21,19,22)	108.0853	D(13,7,18,27)	–4.0841
A(2,3,5)	114.1399	D(1,2,3,6)	–60.3070	A(17,23,24)	108.5811	D(13,7,18,30)	168.2596
A(2,3,6)	123.1022	D(4,2,3,5)	–56.6689	A(17,23,25)	111.9709	D(7,8,9,11)	–138.6872
A(5,3,6)	122.0782	D(4,2,3,6)	114.0467	A(17,23,26)	110.3142	D(7,8,9,12)	42.9408
A(3,5,13)	109.0506	D(2,3,5,13)	40.5136	A(24,23,25)	107.9920	D(10,8,9,11)	48.0413
A(3,5,15)	105.0680	D(2,3,5,15)	149.4819	A(24,23,26)	108.8120	D(8,7,13,34)	–57.4738
A(3,5,17)	115.9915	D(2,3,5,17)	–95.1646	A(25,23,26)	109.0923	D(8,7,13,36)	125.1120
A(13,5,15)	102.2294	D(6,3,5,13)	-130.3084	A(17,27,18)	121.0799	D(18,7,13,5)	46.7492
A(13,5,17)	117.6976	D(6,3,5,15)	–21.3401	A(17,27,28)	107.0759	D(10,8,9,12)	–130.3306
A(15,5,17)	104.9356	D(6,3,5,17)	94.0134	A(17,27,29)	107.5290	D(8,9,11,16)	178.7971
A(8,7,13)	112.0390	D(3,5,13,7)	168.2428	A(18,27,28)	108.7851	D(12,9,11,16)	–3.1193
A(8,7,18)	124.5830	D(3,5,13,34)	77.3148	A(18,27,29)	103.3396	D(5,13,34,35)	162.1007
A(13,7,18)	122.9082	D(3,5,13,36)	–101.3154	A(28,27,29)	108.5014	D(5,13,34,38)	–89.3600
A(7,8,9)	111.1706	D(15,5,13,7)	57.3721	A(18,30,31)	113.4018	D(7,13,34,35)	75.3134
A(7,8,10)	123.7798	D(15,5,13,34)	–33.5559	A(18,30,32)	109.4685	D(7,13,34,38)	–176.1473
A(9,8,10)	124.6848	D(15,5,13,36)	147.8139	A(18,30,33)	108.8436	D(35,34,36,37)	–56.6735
A(8,9,11)	118.1185	D(17,5,13,7)	–56.9351	A(31,30,32)	108.3531	D(38,34,36,37)	52.0060
A(8,9,12)	113.2002	D(17,5,13,34)	–147.8631	A(31,30,33)	109.4591	D(5,13,36,37)	141.4856
A(11,9,12)	128.6572	D(17,5,13,36)	33.5067	A(32,30,33)	107.1265	D(7,13,36,37)	–131.6009
A(9,11,16)	110.4917	D(3,5,17,19)	–82.5930	A(13,34,35)	106.0323	D(5,17,19,20)	178.4848
A(5,13,7)	86.8738	D(3,5,17,23)	38.5607	A(13,34,38)	100.7244	D(5,17,19,21)	–62.0692
A(5,13,34)	83.3599	D(3,5,17,27)	158.0349	A(35,34,38)	104.4100	D(5,17,19,22)	58.8549
A(5,13,36)	94.1253	D(13,5,17,19)	145.6427	A(13,36,37)	108.0075	D(23,17,19,20)	57.3215
A(7,13,34)	90.5590	D(13,5,17,23)	–93.2037			D(23,17,19,21)	176.7675
A(7,13,36)	90.6648	D(13,5,17,27)	26.2705			D(23,17,19,22)	–62.3084
A(5,17,19)	107.4456	D(15,5,17,19)	32.8353			D(27,17,19,20)	–61.9570
A(5,17,23)	110.8023	D(15,5,17,23)	153.9890			D(27,17,19,21)	57.4889
A(5,17,27)	109.9967	D(15,5,17,27)	–86.5369			D(27,17,19,22)	178.4131
A(19,17,23)	110.7869	D(13,7,8,9)	–49.5523			D(5,17,23,24)	178.0824
A(19,17,27)	109.7057	D(13,7,8,10)	123.7914			D(5,17,23,25)	–62.7732
A(23,17,27)	108.1062	D(18,7,8,9)	122.7561			D(5,17,23,26)	58.9252
A(7,18,27)	119.3088	D(18,7,8,10)	–63.9002			D(19,17,23,24)	–62.7576
A(7,18,30)	124.1952	D(8,7,13,5)	–140.7927			D(19,17,23,25)	56.3868
A(27,18,30)	116.0851					D(19,17,23,26)	178.0852

Table 4. (Contd.)

Dihedral angles, deg		Dihedral angles, deg	
D(27,17,23,24)	57.4792	D(7,18,27,17)	–49.3017
D(27,17,23,25)	176.6236	D(7,18,27,28)	–173.8546
D(27,17,23,26)	–61.6780	D(7,18,27,29)	70.9865
D(5,17,27,18)	33.4418	D(30,18,27,17)	137.7460
D(5,17,27,28)	158.7862	D(30,18,27,28)	13.1931
D(5,17,27,29)	–84.7808	D(30,18,27,29)	–101.9658
D(19,17,27,18)	–84.5417	D(7,18,30,31)	–13.2443
D(19,17,27,28)	40.8027	D(7,18,30,32)	107.8794
D(19,17,27,29)	157.2357	D(7,18,30,33)	–135.3339
D(23,17,27,18)	154.5466	D(27,18,30,31)	159.3237
D(23,17,27,28)	–80.1091	D(27,18,30,32)	–79.5527
D(23,17,27,29)	36.3239	D(27,18,30,33)	37.2340

suggest the most probable planar structure of this metallochelate node for Ni(II) and Cu(II) complexes. As to heteroligand Co(III) complex with 4,6,6-trimethyl-2,8-dithio-3,7-diazanonene-4-dithioamide-1,9, water molecule and OH^- anion in the inner coordination sphere, its metallochelate node MN_2S_2 in contrast to Co(II) complex is practically planar; two donor nitrogen atoms, two donor sulfur atoms and two donor oxygen atoms coordinated with Co(III) are located in the apex of coordination octahedron, which is a typical polyhedron for this complex forming atom. Therewith, the Co–N bonds in this complex are shorter than in Co(II) complex and, that is typical, differ noticeable from each other (202.8 and 196.9 pm), while Co–S bonds, on the contrary, are slightly longer (228.6 and 227.1 pm) and also are different. Noteworthy also that Co–O bonds in this complex (207.2 pm with the oxygen atom of H_2O molecule and 183.1 pm with the oxygen atom of hydroxide ligand) are shorter than both Co–S and Co–N bonds. We note also small elongation of O–H bonds in the coordinated water and OH^- anion (98.0 pm and 97.0 pm respectively) as compared with the same in non-coordinated moieties (95.7 pm and 96.0 pm respectively). The additional six-membered chelate ring in this complex is also not planar, although degree of its deviation from the coplanarity is less than in the Co(II), Ni(II) and Cu(II) complexes (Fig. 4). As expectable, the ground state of this complex is spin singlet; it is interesting that according to our

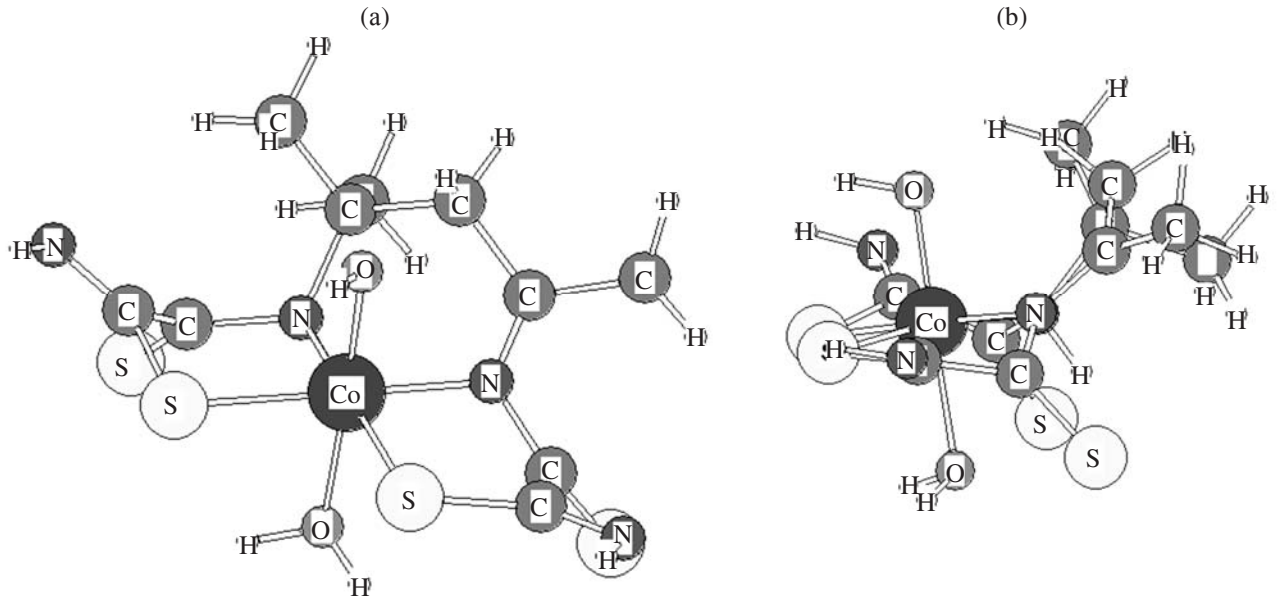


Fig. 4. Steric structure of heteroligand "template" complex of Co(III) with 4,6,6-trimethyl-2,8-dithio-3,7-diazanonene-4-dithioamide-1,9, aqua- and hydroxo-ligands: (a) front view (b) side view.

calculations the complex of same composition to be formed in correspondence with equation (4) with spin multiplicity in ground state $M_S = 5$ can not exist in principle: formation of H_2O–Co(III) donor–acceptor bond in this variant is energetically disadvantageous.

Method of Calculation

For the calculations we applied hybrid method of density functional B3LYP with standard basis set 6-31G(d), based on the coupling of Hartree–Fock method and theory of density functional [8]. The calculations were conducted using Gaussian 98 program [9]. Each internal AO of the basic set was described by six Gauss type functions (GTO), each valent *s*-AO by three GTO, valent *p*-AO by one GTO with adding to each *p*-function of polarization *d*-GTO. Consistence of the found stationary points with the energy minima in each case was proven by calculation of Hessian. Preliminary testing of this method on the examples of different metallochelate complexes of 3*d* elements showed that it allows enough reliable calculate the basic geometric parameters of their structures (Cartesian coordinates of all atoms, interatomic bond lengths, bond angles and dihedral angles).

All the calculations were carried out in the Supercomputer Center of Kazan Scientific Center of the Russian Academy of Sciences.

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