Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1992, **2**(1), 30–32
Mendeleev Communications

Direct Evidence for Bidentate Character of Potentially Tridentate N,S-Ligands. Molecular Structures of Bis[*N*-(2-pyridyl)thiosalicylidene-κ*S*-amino-κ*N*]nickel(II) and Bis{1-isopropyl-3-methyl-4-[*N*-(2-pyridyl)imino-κ*N*-methyl]pyrazole-5-thiolato-κ*S*}copper(II)

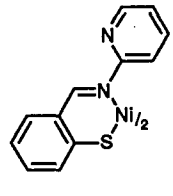
Alexander E. Mistryukov,[a] Igor S. Vasil'chenko,[b] Vladimir S. Sergienko,*[a] Alexander L. Nivorozhkin,[b] Stanislav G. Kochin,[b] Mikhail A. Porai-Koshits,[a] Leonid E. Nivorozhkin[b] and Alexander D. Garnovskii[b]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117090 Moscow, Russia. Fax: +7 095 938 2156*

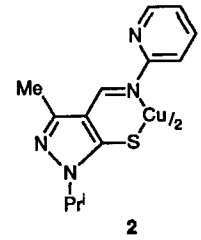
[b] *Institute of Physical and Organic Chemistry, Rostov State University, 344104 Rostov-on-Don, Russia*

Two novel metal chelates with MN_2S_2 coordination: bis[*N*-(2-pyridyl)thiosalicylidene-κ*S*-amino-κ*N*]nickel(II) **1** and bis{1-isopropyl-3-methyl-4-[*N*-(2-pyridyl)imino-κ*N*-methyl]pyrazole-5-thiolato-κ*S*}copper(II) **2** have been investigated; both contain an additional potentially active nitrogen centre in the α-pyridyl substituents on the imino groups, but X-ray structural investigation shows that in neither case is the pyridyl nitrogen atom coordinated to the metal; complex **1** has a slightly distorted *cis*-planar configuration with a dihedral angle between the NNiS and N′NiS′ planes of 13.5° and a shortened S···S distance, 2.864(5) Å, while the Cu atom in **2** has a *cis*-distorted tetrahedral coordination [dihedral angle between NCuS and N′CuS′ planes 57.6°, S···S distance 3.178(4) Å].

In recent years variations in the structures of Schiff base complexes containing potentially active groups for additional coordination,[1–6] including the pendant-arm macrocycles,[7] have been extensively studied. Evidence for the presence of extra-coordination in solution was obtained for *N*-(2-pyridyl)salicylideneaminato complexes of Ni^{II}, Cu^{II} and Co^{II}.[1,2] The coordination of an N(Py) atom to a neighbouring metal atom leading to oligomerization of a complex was established in the crystal structure of tetrameric $[(salPy)Cu(NO_3)H_2O]_4$.[3] Intramolecular coordination to the same metal atom (tridentate chelating coordination) has been reported in only one case: the crystal structure of the pentacoordinated bis[2-mercapto-5-ethyl-3-*N*-



1



2

(2-pyridyl)thienylideneaminato]cobalt(II), where one of two ligands acts in a tridentate fashion, with Co—N(Py) distance 2.448 Å.[4] In this structure the configuration of the Co-polyhedron was described as intermediate between a trigonal bipyramid and a tetragonal pyramid or as a monocapped tetrahedron. A recent structural investigation of bis[*N*-(2-pyridyl)salicylideneaminates] of copper(II)[5] showed them to have a tetracoordinated Cu^{II} atom. That means that the N(Py) atom does not take part in coordination of the metal.

In the present paper X-ray studies† of two novel metal chelates **1** and **2** with MN_2S_2 coordination sphere have been performed. Both compounds contain a potential donor nitrogen centre in the α-pyridyl substituents at their coordinated imino groups.

Compound **1** was prepared by template condensation of bis[thiosalicylaldehydato]nickel(II)[8] with 2-aminopyridine in chloroform; compound **2** was prepared according to ref. 9. The crystals used for the X-ray study were obtained by slow crystallization from a chloroform–hexane (1:1) mixture for **1** and from methanol for **2**.

As shown by magnetic susceptibility measurements, complex **1** is diamagnetic both in the solid state and in chloroform solution. The magnetic moment of complex **2** in the solid state is 1.72 μ_B at 280 K.

In compound **1** the nickel atom has a slightly distorted *cis*-planar N_2S_2 environment (Fig. 1), which is a characteristic feature of the Ni^{II} thiosalicyliminates with sterically non-bulky substituents.[10] The dihedral angle between the S(1)NiN(11) and S(2)NiN(21) planes is 13.5°. Metallocycles C_3NSNi have an 'envelope' conformation with the bending along the N—S axis of 21.4° and 44.7° for different rings within the same molecule. Owing to this bending the whole molecule has a stepped structure. The dihedral angle between the planar (±0.02 Å) pyridine rings is 11.9°. The pyridine nitrogen atoms are not coordinated to the nickel. As in other planar N_2S_2 complexes,[11,12] the S···S distance of 2.864(5) Å is much shorter than the distance corresponding to double the van der Waals radius of sulphur (3.70 Å).[13]

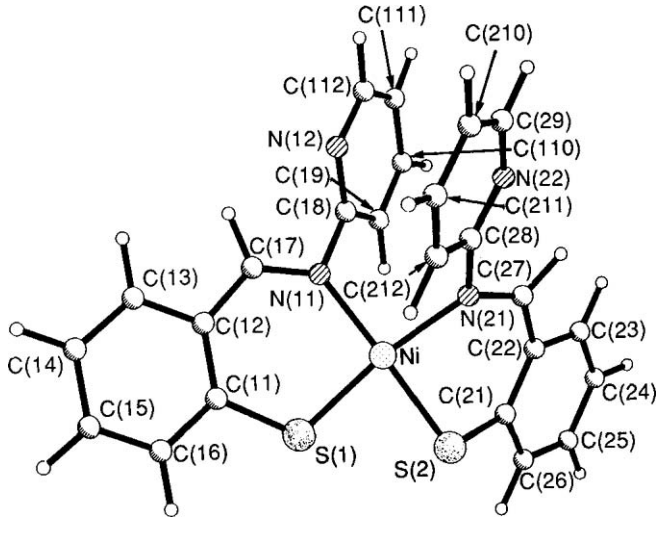


Fig. 1 Structure of complex **1**. Selected bond lengths (Å) and valence angles (°): Ni–S(1) 2.146(4), Ni–S(2) 2.162(3), Ni–N(11) 1.92(1), Ni–N(21) 1.94(1); S(1)NiS(2) 83.3(1), S(1)NiN(11), 95.3(3), S(1)NiN(21) 167.7(3), S(2)NiN(11) 170.1(3), S(2)NiN(21) 90.2(3), N(11)NiN(21) 92.8(4).

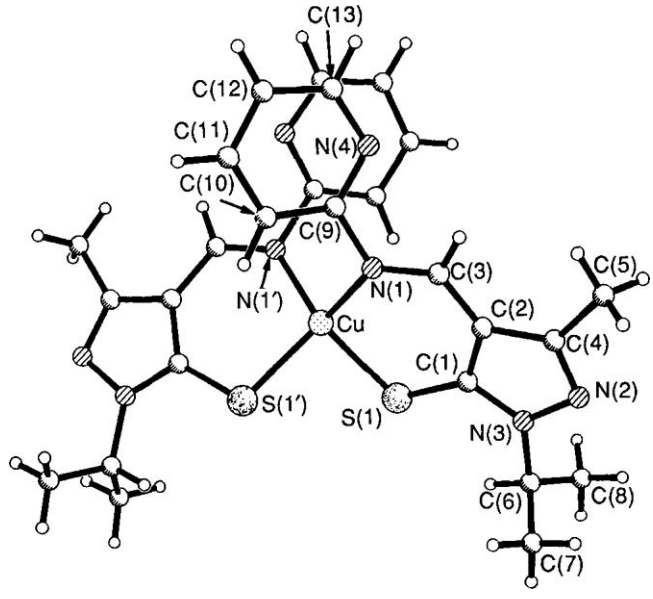


Fig. 2 Structure of complex **2**. Selected bond lengths (Å) and valence angles (°): Cu–S(1) 2.230(2), Cu–N(1) 1.982(5); S(1)CuN(1) 100.2(2), S(1)CuS(1') 90.92(8), N(1)CuN(1') 100.3(2).

The parameters of the EPR spectra of complex **2** in chloroform–toluene (1:1) solution [$g_0 = 2.076 \pm 0.005$; $A_0 = (50.4 \pm 0.2) \times 10^{-4}$ cm^{-1}] and related frozen glass [$g_\parallel = 2.149 \pm 0.005$; $A_\parallel = (131.3 \pm 0.2) \times 10^{-4}$ cm^{-1}; $g_\perp = 2.036 \pm 0.005$; $A_\perp = (17.0 \pm 0.2) \times 10^{-4}$ cm^{-1}] are consistent with those obtained for other essentially planar to tetrahedral distorted structures.[14]

In the crystal structure of compound **2** (Fig. 2) the copper atom located on the two-fold axis has a significantly *cis*-distorted tetrahedral N_2S_2 environment with an angle between the planar (±0.036 Å) metallocycles of 57.6° and shortened S···S contacts of 3.178 Å. The planar (±0.009 Å) pyridyl substituents are rotated around the C—N bonds by 45.5°, relative to the plane of the metallocycles. As in complex **1**, the pyridine nitrogen atoms do not coordinate the metal.

As shown previously for nickel metallochelates, the annelation of the pyrazole ring to a chelate ring in Schiff base complexes stabilizes the tetrahedral structure.[9] The structure of complex **2** shows that this tendency also operates for copper(II) metallochelates since neither aryl[15] nor pyridyl[5] substituents at the coordinated imino group lead to the replacement of the planar coordination by a tetrahedral one.

An analysis of the bond lengths in metallocycles **1** and **2** reveals that in both cases the ligands are in a delocalized iminothiolic tautomeric form.[16]

Received: Moscow, 10th September 1991
Cambridge, 8th November 1991; Com. 1/04777I

References

1 P. S. K. China and S. E. Livingstone, *Austr. J. Chem.*, 1969, **22**, 1613.

† *Crystal data* for **1**: $C_{24}H_{18}N_4S_2Ni$, $M = 485.2$, monoclinic, space group Cc, $a = 16.000(3)$ Å, $b = 16.551(4)$ Å, $c = 8.420(2)$ Å, $\beta = 103.50(2)°$, $U = 2168.2(8)$ Å^3, $Z = 4$, $D_c = 1.49$ g cm^{-3}. Monochromatized Mo-Kα radiation, $\lambda = 0.7107$ Å, $\mu = 11.0$ cm^{-1}. Final R and R_w are 0.052 and 0.046 respectively, for 1206 reflections having $I \geq 2\sigma(I)$.

For **2**: $C_{26}H_{28}N_8S_2Cu$, $M = 580.2$, monoclinic, space group $C2/c$, $a = 21.007(8)$ Å, $b = 9.341(3)$ Å, $c = 18.620(8)$ Å, $\beta = 128.26(2)°$, $U = 2869(2)$ Å^3, $Z = 4$, $D_c = 1.34$ g cm^{-3}. Monochromatized Mo-Kα radiation, $\lambda = 0.7107$ Å, $\mu = 9.3$ cm^{-1}. Final R and R_w are 0.044 and 0.043 respectively, for 1131 reflections having $I \geq 2\sigma(I)$.

Intensity data were collected at room temperature on a Syntex $P2_1$ diffractometer by the $\omega/2\theta$ scan method. The structures were solved by the Patterson method (SHELX). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, Issue No. 1, 1992.

2 R. K. Parashar, R. C. Sharma, A. Kumar and G. Mohan, *Inorg. Chim. Acta*, 1988, **151**, 201.
3 J. Drummond and J. S. Wood, *J. Chem. Soc., Dalton Trans.*, 1972, 365.
4. L. M. Shkolnikova, S. S. Makarevich, V. E. Zavodnic, M. A. Kalik and Ya. L. Goldfarb, *Koord. Khim.*, 1976, **2**, 115. [*Sov. J. Coord. Chem.* (*Engl. Transl.*), 1976, **2**, 93].
5. A. Castineiras, J. A. Castro, M. L. Duran, J. A. Garcia-Vazquez, A. Macias, J. Romero and A. Sousa, *Polyhedron*, 1989, **21**, 2543.
6. N. M. Atherton, D. E. Fenton, G. J. Hewson, C. H. McLean, R. Bastida, J. Romero, A. Sousa and E. E. Castellano, *J. Chem. Soc., Dalton Trans.*, 1988, 1059.
7. H. Adams, N. A. Bailey, W. D. Carlisle and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1990, 1271.
8. E. Hoyer and B. Lorenz, *Z. Chem.*, 1968, **8**, 28.
9. L. E. Nivorozhkin, M. S. Korobov, A. L. Nivorozhkin, L. E. Konstantinovskii and V. I. Minkin, *Zh. Obsch. Khim.*, 1985, **55**, 1125.
10. V. A. Kogan, N. N. Kharabaev, O. A. Osipov and S. G. Kochin, *Zh. Strukt. Khim.*, 1981, **22**, 126 [*J. Struct. Chem.* (*Engl. Transl.*), 1981, **22**, 96].
11. O. A. Dyachenko, L. O. Atovmian and S. M. Aldoshin, *J. Chem. Soc., Chem. Commun.*, 1975, 105.
12. O. A. Dyachenko, L. O. Atovmian, S. M. Aldoshin, V. A. Kogan, S. G. Kochin and O. A. Osipov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 2130 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, 2019).
13. L. Pauling, *The Nature of the Chemical Bond*, 2nd edn., Cornell University Press, Ithaca, New York, 1945.
14. O. P. Andersen, J. Becher, M. Frydendahl, L. F. Taylor and H. Toftlund, *J. Chem. Soc., Chem. Commun.*, 1986, 699.
15. G. V. Panova, N. K. Vikulova and V. M. Potapov, *Usp. Khim.*, 1980, **49**, 1234 (*Russ. Chem. Rev.*, 1980, **49**, 1234).
16. A. L. Nivorozhkin, E. V. Sukolenko, L. E. Nivorozhkin, N. I. Borisenko, V. I. Minkin, Yu. K. Grishin, O. A. Dyachenko, T. G. Takhirov and D. B. Tagiev, *Polyhedron*, 1989, **8**, 569.