

the mean C—NH₂ bond lengths for ligands *A* and *B* [1.318 (12) and 1.320 (9) Å].

Two of the nitrate ions per molecular unit are in general positions and are planar ($\chi^2 = 2$), while the third is centred on $\bar{1}$ and is disordered. There are eight regions of high electron density around N(2) of the disordered nitrate. Four regions correspond to O(4), O(4)', O(5), O(5)' (primed at \bar{x} , \bar{y} , \bar{z}) each with occupancy $\frac{1}{2}$, and another four correspond to O(6), O(6)', O(7), O(7)' each with occupancy $\frac{1}{4}$. The disordered nitrate is not planar ($\chi^2 = 1445$) with O(4) and O(4)' 0.218 (8) Å from the mean plane. O(5), O(5)', O(6), O(6)', O(7), O(7)' are on the other hand coplanar with N(2) ($\chi^2 = 1$) and with O(4) and O(4)' 0.27 (1) Å from this mean plane. The vibrations of the disordered O atoms were relatively high and their parameters did not converge when refined anisotropically. Isotropic thermal parameters, however, converged to rather high values (5.2–7.5 Å²).

The coordination polyhedron is closer to a perfect square antiprism (D_{4d}) than to a trigonal-faced dodecahedron (D_{2d}) or a cube (O_h). This conclusion is based on the shape-parameter considerations (Muetterties & Guggenberger, 1974) reported in Table 5 (deposited). The bidentate ligands span *m* edges of the idealized eight-coordination polyhedron with O(1A) and O(1B) at the *A* site and O(2A) and O(2B) at the *B* site of the *BAAB* trapezoids. The twist angles in the two *BAAB* trapezoids, ϕ , defined to be the dihedral angle between the planes *A*, *A*, and the centroid of the two *B* positions, and *B*, *B*, and the centroid of the two *A* positions, are 30.6 and 26.3°, much closer to the D_{4d} (24.5°) than the D_{2d} (0.0°) case. The dihedral angles along the dodecahedral *b* edges, δ_b , are 4.4° and 60.9° compared with the theoretical D_{4d} angles (0.0 and

52.4°), and the theoretical D_{2d} angles (29.5 and 29.5°). The coordination polyhedron is strikingly different from the one found in tetrakis(tironato)cerate(IV) (Haddad & Raymond, 1986), where the bidentate ligands span the *m* edges of an almost regular trigonal-faced dodecahedron (D_{2d}).

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Structure of the Mixed-Valence Compound Poly{[*N,N*-bis(3,5-dimethyl-1-pyrazolylmethyl)aminobenzene]-tris(μ -thiocyanato-*S,N*)-dicopper(I,II)}

BY WILLEM L. DRIESSEN,* HENK L. BLONK, WINFRIED HINRICHS† AND JAN REEDIJK

Department of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

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Abstract. [Cu₂(C₁₈H₂₃N₅)(NCS)₃]_n, $M_r = 610.74$, monoclinic, $P2_1/n$, $a = 13.473$ (1), $b = 21.975$ (2),

$c = 8.666$ (1) Å, $\beta = 92.93$ (1)°, $V = 2562.4$ Å³, $Z = 4$, $D_x = 1.58$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 19.25$ cm⁻¹, $F(000) = 1244$, $T = 293$ K, final $R = 0.028$ for 1624 significant reflections. Each Cu^{II} ion is surrounded by five N atoms in a geometry which is very close to square pyramidal. The deviation from a square pyramid is largely due to the constraint of the ligand

* To whom correspondence should be addressed.

† Present address: Institute of Crystallography, Department of Chemistry, Free University of Berlin, 1000 Berlin 33, Federal Republic of Germany.

(pabd). The Cu^{II} ion binds to the aniline N atom [2.161 (4) Å] and the two pyrazole N atoms [1.978 (5) and 1.997 (5) Å] and to the N atoms [1.945 (5) and 2.172 (6) Å] of the thiocyanate anions which also bind, through their S atoms, to two different Cu^I ions. Each Cu^I ion is surrounded by three S atoms [2.328 (2), 2.407 (2) and 2.443 (2) Å] and one N atom [1.984 (6) Å] of the thiocyanate anions in a distorted tetrahedral geometry. Two of the thiocyanate anions bridge to another Cu^I ion and the other two to different Cu^{II} ions. A two-dimensional network of Cu(pabd)²⁺ and Cu⁺ ions is formed through the bridging of these cations by the SCN⁻ ions.

Introduction. Bis(3,5-dimethyl-1-pyrazolylmethyl)-aminobenzene (abbreviated pabd) forms a variety of complexes with transition-metal ions. The synthesis and characterization of these compounds has been described earlier (Blonk, Driessen & Reedijk, 1985).

The mixed copper(I)-copper(II)-thiocyanate compound, described in this paper, formed from a starting solution which initially only contained divalent copper. The solvent, methanol, probably played a role in this spontaneous reduction.

The stereochemistry of this compound could not be deduced fully from spectroscopic data alone (Blonk *et al.*, 1985): The ligand field spectrum indicated a five- or a six-coordinated Cu^{II} geometry. The infrared data indicated that the aniline N atom takes part in the coordination and that two different NCS species are present: either one monodentate N-bonded and one bridging bidentate NCS species or two differently bridging bidentate NCS species.

Experimental. Dark-green needle grown from methanol at room temperature with approximate dimensions 0.4 × 0.1 × 0.1 mm. Enraf-Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo K α . Cell constants from setting angles of 24 reflections. Corrections for Lorentz and polarization effects. No absorption correction applied (transmission coefficients 0.95 to 1.04). $\theta_{\max} = 22^\circ$ (very few significant reflections with $\theta > 22^\circ$), h 0 to 14, k 0 to 23, l -9 to 9. Standard reflections $39\bar{2}$, $3\bar{9}2$ and $63\bar{2}$, intensity variation 5.5%. 3401 measured reflections, 3239 independent, $R_{\text{int}} = 0.034$, 1615 with $I < 2\sigma(I)$.

Structure solved by heavy-atom method. F used in LS refinement. Some of the H atoms found in difference Fourier maps, the others placed at 0.96 Å from the parent atoms. Least-squares refinement of non-H-atom positional and anisotropic thermal parameters; positional parameters of H atoms coupled to parent atoms; fixed isotropic thermal factor of 5.15 Å² for the H atoms. Final $R = 0.028$, $S = 1.110$, $w = 1/\sigma^2(F)$, $wR = 0.034$, $\Delta_{\max}/\sigma < 0.20$. Max., min. $\Delta\rho$ excursions in final difference synthesis 0.23, -0.20 e Å⁻³. Scattering factors and anomalous-dis-

persion corrections from *International Tables for X-ray Crystallography* (1974). Leiden University Computer (Amdahl V7B); programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

Table 1. Atomic coordinates (Cu^I and Cu^{II} × 10⁵, others × 10⁴) and equivalent isotropic thermal parameters (Cu^I and Cu^{II} Å² × 10², others Å² × 10) of the non-H atoms with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \pi^2 \text{trace } U.$$

	x	y	z	B _{eq}
Cu ^I	38368 (7)	7014 (4)	31940 (10)	516 (3)
Cu ^{II}	21888 (5)	26917 (3)	6653 (8)	305 (2)
S(1)	4030 (1)	1748 (1)	2924 (2)	59 (1)
C(2)	5035 (4)	1946 (2)	3878 (6)	33 (2)
N(3)	5753 (4)	2107 (2)	4525 (6)	45 (2)
S(4)	2471 (2)	580 (1)	1318 (3)	73 (1)
C(5)	2245 (4)	1301 (3)	940 (7)	40 (2)
N(6)	2113 (3)	1808 (2)	697 (5)	41 (1)
S(7)	3234 (1)	410 (1)	5700 (2)	45 (1)
C(8)	4235 (5)	52 (2)	6365 (6)	40 (2)
N(9)	4928 (4)	-210 (2)	6809 (6)	49 (2)
N(10)	2520 (3)	3653 (2)	783 (5)	27 (1)
C(11)	3514 (4)	3818 (2)	1475 (6)	31 (2)
C(12)	3818 (5)	4409 (3)	1453 (9)	63 (2)
C(13)	4746 (6)	4563 (3)	2073 (10)	83 (3)
C(14)	5357 (5)	4129 (3)	2712 (8)	58 (2)
C(15)	5049 (4)	3544 (3)	2746 (7)	45 (2)
C(16)	4112 (4)	3390 (2)	2144 (6)	36 (2)
C(20)	1703 (4)	3893 (2)	1657 (6)	35 (2)
N(21)	1597 (3)	3486 (2)	2964 (5)	34 (1)
N(22)	1727 (3)	2875 (2)	2745 (5)	37 (1)
C(23)	1491 (5)	2612 (3)	4064 (7)	45 (2)
C(24)	1204 (5)	3047 (3)	5084 (7)	54 (2)
C(25)	1262 (5)	3599 (3)	4382 (7)	46 (2)
C(26)	1529 (5)	1945 (3)	4327 (8)	64 (2)
C(27)	989 (6)	4217 (3)	4882 (7)	66 (3)
C(30)	2434 (4)	3813 (2)	-878 (6)	31 (2)
N(31)	3022 (3)	3380 (2)	-1646 (5)	32 (1)
N(32)	2972 (3)	2785 (2)	-1215 (5)	32 (1)
C(33)	3563 (4)	2489 (3)	-2143 (7)	43 (2)
C(34)	3959 (5)	2888 (3)	-3158 (7)	53 (2)
C(35)	3611 (5)	3455 (3)	-2838 (7)	43 (2)
C(36)	3711 (5)	1816 (3)	-2006 (8)	64 (2)
C(37)	3790 (6)	4049 (3)	-3567 (8)	71 (3)

Table 2. Bond lengths (Å) and selected angles (°) with e.s.d.'s in parentheses

Cu ^I -S(1)	2.328 (2)	C(12)-C(13)	1.38 (1)
Cu ^I -S(4)	2.407 (2)	C(13)-C(14)	1.36 (1)
Cu ^I -S(7)	2.443 (2)	C(14)-C(15)	1.351 (9)
Cu ^I -N(9)	1.984 (6)	C(15)-C(16)	1.384 (8)
Cu ^{II} -N(6)	1.945 (5)	C(20)-N(21)	1.455 (7)
Cu ^{II} -N(10)	2.161 (4)	N(21)-N(22)	1.369 (6)
Cu ^{II} -N(22)	1.978 (5)	N(21)-C(25)	1.353 (8)
Cu ^{II} -N(32)	1.997 (5)	N(22)-C(23)	1.334 (8)
Cu ^{II} -N(3)	2.172 (6)	C(23)-C(24)	1.371 (9)
S(1)-C(2)	1.610 (7)	C(23)-C(26)	1.485 (9)
C(2)-N(3)	1.149 (7)	C(24)-C(25)	1.360 (9)
S(4)-C(5)	1.643 (7)	C(25)-C(27)	1.477 (9)
C(5)-N(6)	1.147 (7)	C(30)-N(31)	1.424 (7)
S(7)-C(8)	1.641 (8)	N(31)-N(32)	1.364 (6)
C(8)-N(9)	1.146 (7)	N(31)-C(35)	1.344 (8)
N(10)-C(11)	1.483 (7)	N(32)-C(33)	1.329 (7)
N(10)-C(20)	1.466 (7)	C(33)-C(34)	1.370 (9)
N(10)-C(30)	1.480 (7)	C(33)-C(36)	1.496 (9)
C(11)-C(12)	1.361 (8)	C(34)-C(35)	1.364 (9)
C(11)-C(16)	1.350 (8)	C(35)-C(37)	1.475 (9)
S(1)-Cu ^I -S(4)	97.31 (7)	N(6)-Cu ^{II} -N(32)	98.3 (2)
S(1)-Cu ^I -S(7)	113.09 (8)	N(6)-Cu ^{II} -N(3)	99.4 (2)
S(1)-Cu ^I -N(9)	116.1 (2)	N(10)-Cu ^{II} -N(22)	80.3 (2)
S(4)-Cu ^I -S(7)	107.08 (9)	N(10)-Cu ^{II} -N(32)	79.7 (2)
S(4)-Cu ^I -N(9)	123.5 (2)	N(10)-Cu ^{II} -N(3)	90.0 (2)
S(7)-Cu ^I -N(9)	100.1 (2)	N(22)-Cu ^{II} -N(32)	157.9 (2)
N(6)-Cu ^{II} -N(10)	170.6 (2)	N(22)-Cu ^{II} -N(3)	93.4 (2)
N(6)-Cu ^{II} -N(22)	99.8 (2)	N(32)-Cu ^{II} -N(3)	95.9 (2)

Discussion. Positional parameters and isotropic thermal parameters for the non-H atoms are listed in Table 1.* Bond distances of the non-H atoms and selected angles are given in Table 2. An ORTEP projection (Johnson, 1965) of two molecular entities $\text{Cu}_2(\text{pabd})(\text{NCS})_3$, related through an inversion centre, is shown in Fig. 1. An impression of the network which is formed by the bridging of the thiocyanate anions between the Cu^{II} and Cu^{I} ions is given in Fig. 2.

From the stoichiometry of the compound it was inferred that half of the Cu ions are present in the monovalent state and the other half in the divalent state. However, from the X-ray data alone it cannot be decided which of the two metal ions in the asymmetric unit is Cu^{II} and which is Cu^{I} . From the preference of Cu^{I} for a tetrahedral rather than a square-pyramidal coordination geometry and from the preference of Cu^{II}

for S donor atoms rather than N donor atoms, a very good guess of which is which can be made (see Table 1 and Fig. 1). This guess is substantiated by the EPR data (Blonk *et al.*, 1985), which are in accordance with a square-pyramidal N_5 environment (Hathaway & Billing, 1970).

Calculation of the structural index τ (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984) on the basis of atoms N(22), N(10), N(32) and N(6) gives a value of 0.16. This value is closer to square pyramidal ($\tau=0.0$) than to trigonal bipyramidal ($\tau=1.0$). It can even be considered as too high, since it is mainly determined by the N(22)— Cu^{II} —N(32) angle of 160° , which is largely dictated by the constraint of the ligand. In all compounds with pyrazole-substituted amine ligands, the bite of the ligand is such that the amine N—metal—pyrazole N angle is significantly smaller than 90° . This angle is about 80° for Co^{II} , Ni^{II} and Cu^{II} and about 70° for Mn^{II} and Cd^{II} (Blonk *et al.*, 1985; van Driel, Driessen & Reedijk, 1985; Hulsbergen, Driessen, Reedijk & Verschoor, 1984; Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985; Veldhuis, Driessen & Reedijk, 1986). In the present compound the N(10)— Cu^{II} —N(22) and N(10)— Cu^{II} —N(32) angles are also close to 80° (see Table 2).

The geometry around Cu^{II} in the related compound $\text{Cu}(\text{bpae})\text{Br}_2$ [bpae = bis(1-pyrazolylmethyl)aminoethane] is also square pyramidal, with one of the coordinating Br ions apical (Velduis *et al.*, 1986). In contrast, the geometry around Cu^{II} in the even more closely related $\text{Cu}(\text{pabd})\text{Br}_2$ is trigonal bipyramidal, with the two coordinating Br ions and the amine N atoms forming the trigonal plane (Blonk *et al.*, 1985). The factors governing the geometry are not clear, although differences in the packing may play a role. From the infrared data it was concluded that the aniline N atom took part in the coordination (Blonk *et al.*, 1985), which indeed is the case. The angles around the aniline N atom [N(10)] do not diverge much from tetrahedral [max. deviation $\text{Cu}-\text{N}(10)-\text{C}(30)$ $100.4(3)^\circ$]. From infrared data on this compound it was also inferred (Blonk *et al.*, 1985) that two different thiocyanate species must be present. Indeed, there are two differently bridging NCS^- species. One NCS^- ion bridges two Cu^{I} ions and the other two NCS^- ions bridge a Cu^{II} ion and a Cu^{I} ion. However, the differences in bond lengths and angles between the three NCS^- ions is only very slight, the largest difference being between the ion $\text{S}^1\text{C}^2\text{N}^3$ (bridging Cu^{I} and Cu^{II}) on the one hand and the ions $\text{S}^4\text{C}^5\text{N}^6$ (also bridging Cu^{I} and Cu^{II}) and $\text{S}^7\text{C}^8\text{N}^9$ (bridging two Cu^{I} 's) on the other (see Fig. 1 and Table 2).

The phenyl ring and the pyrazole rings are planar [largest deviation from the least-squares planes $0.013(5) \text{ \AA}$]. The pyrazole rings make angles of $86.0(3)$ and $105.8(3)^\circ$ with the phenyl ring, and an angle of $19.8(3)^\circ$ with one another.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44053 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

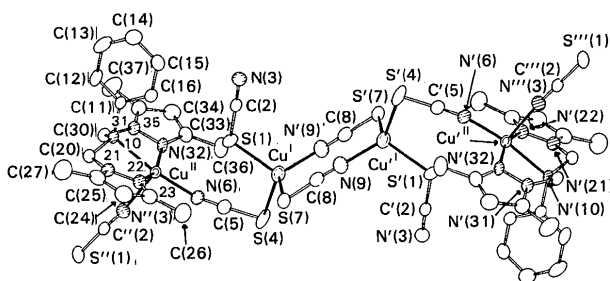


Fig. 1. ORTEP projection (Johnson, 1965) and atomic labelling of twice the molecular entity $\text{Cu}_2(\text{pabd})(\text{NCS})_3$, related through an inversion centre. For clarity the H atoms are omitted. N(10), N(21), N(22), C(23), N(31) and C(35) are indicated by numerals only.

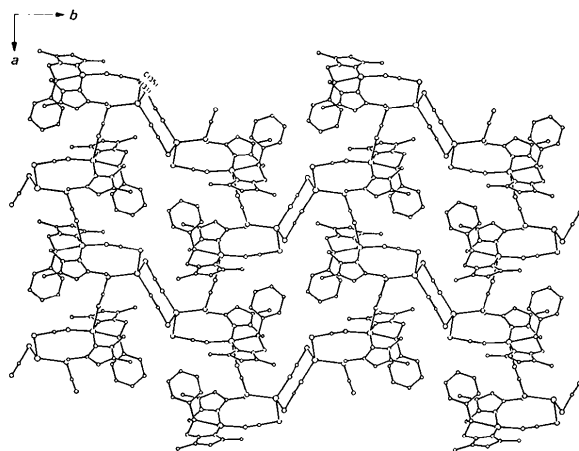


Fig. 2. Projection on the ab plane of the two-dimensional network of $\text{Cu}(\text{pabd})^{2+}$ and Cu^{I} ions linked by SCN^- ions.

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Structure of Hexakis(acetonitrile)nickel(II) Hexafluoroantimonate(V)

BY I. LEBAN, D. GANTAR AND B. FRLEC

Jožef Stefan Institute, E. Kardelj University, 61001 Ljubljana, Yugoslavia

AND D. R. RUSSELL AND J. H. HOLLOWAY

Chemistry Department, The University, Leicester LE1 7RH, England

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Abstract. [Ni(NCCH₃)₆][SbF₆]₂, $M_r = 776.5$, rhombohedral, $R\bar{3}$, $a = 8.764(2)\text{Å}$, $\alpha = 80.92(2)^\circ$, $V = 650.3\text{Å}^3$, $Z = 1$, $D_x = 1.983\text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069\text{Å}$, $\mu = 30.8\text{ cm}^{-1}$, $F(000) = 370$, $T = 293(1)\text{ K}$, final $R = 0.031$, $wR = 0.039$ for 783 observed reflections [$I > 3\sigma(I)$]. The structure consists of discrete [Ni(NCCH₃)₆]²⁺ cations and [SbF₆]⁻ anions. The Ni (on $\bar{3}$ position) is octahedrally coordinated by the six nitrogens of the acetonitrile ligands [Ni–N distance 2.075(3) Å], whilst Sb (on threefold axis) has six fluorines at distances 1.825(4) and 1.827(4) Å respectively.

Introduction. Metal(II) hexafluoroantimonates of the type $MF_2 \cdot 2SbF_5$ where M is Sn (Birchall, Dean & Gillespie, 1971), Mn, Fe, Ni (Dean, 1975) and Mg, Cr, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb (Gantar, Leban, Holloway & Frlec, 1987) have been prepared and characterized. A single-crystal X-ray study of $AgF_2 \cdot 2SbF_5$ has shown that it contains Ag^{2+} ions in planar coordination with two Ag–F distances at 2.09 and 2.13 Å and two further atoms at 2.43 Å completing a distorted octahedron. The F atoms are associated with distorted [SbF₆]⁻ octahedra in the structure (Gantar, Leban, Holloway & Frlec, 1987).

Recently, we have shown that dissolution of some metal(II) hexafluoroantimonates (metal = M = Cr, Fe, Co, Ni, Cu, Cd, Hg) in acetonitrile gives rise to ternary

adducts of formula $MF_2 \cdot 2SbF_5 \cdot xCH_3CN$ which can be isolated from the solutions. Vibrational spectroscopic data have shown that the acetonitrile in these adducts is coordinated *via* the N (Gantar, Leban, Frlec, Russell & Holloway, in preparation).

Although a variety of fluoro compounds containing coordinated acetonitrile have been reported (*e.g.* Berry, Prescott, Sharp & Winfield, 1977; Halstead, Eller & Eastman, 1979; Hathaway, Holah & Underhill, 1962; Holloway, Laycock & Bougon, 1984) little is known about their crystal structures. Only one simple fluoride structure, $WSF_4 \cdot CH_3CN$ (Holloway, Kaučič & Russell, 1983), appears to have been studied, while others such as [Re(CH₃CN)₃(CO)₃][BF₄] (Chan, Isaacs & Graham, 1977), [Rh(CH₃CN)(PPh₃)₃][BF₄] (Pimblett, Garner & Clegg, 1985) and Co(CH₃CN)₂(PO₂F₂)₂ (Begley, Dove, Hibbert, Logan, Nunn & Sowerby, 1985) are more complex.

Details of the synthesis and spectroscopy of [Ni(NCCH₃)₆][SbF₆]₂ and its relatives, together with X-ray single-crystal data for some of the compounds, will be published separately (Gantar, Leban, Frlec, Russell & Holloway, in preparation).

Experimental. Solid $NiF_2 \cdot 2SbF_5$, prepared as described previously (Gantar, Leban, Holloway & Frlec, 1987), was loaded into a pre-dried and fluorinated Pyrex tube and dried acetonitrile was introduced by distillation.