

Fig. 2. Distribution of the organic groups and water molecules in a plane close to $y=0.5$; H atoms are not shown.

have been drawn in their idealized positions: 0.5, 0, 0 for O(W5) and 0.130, 0.25, 0.315 for O(W6). Fig. 2 shows the distribution of the organic groups and water molecules in the plane $y=0.5$. H atoms are not shown.

A very intricate three-dimensional network of hydrogen bonds is reported in Table 2. The Ca atoms, located on a mirror plane, have a sevenfold coordination made of four O atoms and three water molecules with Ca—O distances ranging from 2.376 to 2.419 Å. Some H atoms belonging to the disordered water molecules could not be located.

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Structure of Bis(2,2'-bipyridyl)thiocyanatocopper(II) Nitrate Monohydrate

BY V. MANRIQUEZ, I. BRITO AND C. ANDRADE

Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

O. WITTKÉ

Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago, Chile

AND H. G. VON SCHNERING AND K. PETERS

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

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Abstract. $[\text{Cu}(\text{NCS})(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$, $M_r = 514.02$, triclinic, $P\bar{1}$, $a = 12.098$ (4), $b = 12.810$ (5), $c = 7.777$ (2) Å, $\alpha = 102.80$ (3), $\beta = 107.56$ (2), $\gamma = 76.03$ (3)°, $V = 1100.6$ (6) Å³, $Z = 2$, $D_m = 1.556$, $D_x = 1.551$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.2183$ mm⁻¹, $F(000) = 526$, $T = 293$ K, $R = 0.041$ for 4104 unique observed reflections. The Cu atom is pentacoordinated to the four N atoms of the bipyridyl ligands and the N atom of the thiocyanato group in a

The high thermal factor observed for the O(W6) water molecule can be explained by considering its surroundings. Within a range of 3.5 Å this molecule has only three neighbours [O(W2), O(W3) and O(W4)] while all the other water molecules either belong to the coordination polyhedron of the Ca atom or are closely connected to an NH₃ group with N—O distances ranging from 2.733 to 2.939 Å.

References

- AVERBUCH-POUCHOT, M. T. & DURIF, A. (1987). *Acta Cryst.* **C43**, 1895–1896.
 AVERBUCH-POUCHOT, M. T. & DURIF, A. (1988). *Acta Cryst.* **C44**, 212–216.
 AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J. C. (1988). In preparation.
 ENRAF-NONIUS (1977). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

near-regular trigonal bipyramidal arrangement, where only three distances differ significantly: 1.992 (2) (average) for the axial bonds, 2.079 (3) (average) and 2.010 (3) Å for the equatorial bonds.

Introduction. This structure determination is a contribution to the study of the chemistry of copper complexes with different donor ligands coordinated by atoms usually found in natural proteins such as N, S and O

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | U_{eq} |
|-------|-----------|-----------|------------|----------|
| Cu | -2120 (1) | -1642 (1) | -4010 (1) | 51 (1) |
| S | -1589 (1) | 1110 (1) | -6726 (1) | 72 (1) |
| N(1) | -3575 (2) | -2388 (2) | -4697 (4) | 48 (1) |
| C(2) | -3691 (3) | -3381 (2) | -5619 (4) | 59 (1) |
| C(3) | -4659 (3) | -3827 (3) | -5827 (5) | 72 (1) |
| C(4) | -5530 (3) | -3241 (3) | -5023 (5) | 78 (2) |
| C(5) | -5428 (3) | -2215 (3) | -4054 (5) | 69 (1) |
| C(6) | -4448 (2) | -1797 (2) | -3928 (4) | 50 (1) |
| C(7) | -4262 (2) | -701 (2) | -2972 (4) | 50 (1) |
| C(8) | -5101 (3) | 81 (3) | -2281 (4) | 64 (1) |
| C(9) | -4855 (3) | 1097 (3) | -1451 (4) | 71 (1) |
| C(10) | -3780 (3) | 1321 (3) | -1320 (5) | 72 (1) |
| C(11) | -2983 (3) | 518 (2) | -2049 (4) | 68 (1) |
| N(12) | -3211 (2) | -475 (2) | -2853 (3) | 53 (1) |
| N(13) | -797 (2) | -1908 (2) | -1632 (3) | 49 (1) |
| C(14) | -772 (2) | -1412 (2) | 85 (4) | 60 (1) |
| C(15) | 159 (3) | -1658 (3) | 1556 (4) | 67 (1) |
| C(16) | 1100 (2) | -2459 (3) | 1260 (4) | 68 (1) |
| C(17) | 1094 (2) | -2983 (2) | -502 (4) | 62 (1) |
| C(18) | 132 (2) | -2687 (2) | -1923 (4) | 48 (1) |
| C(19) | 32 (2) | -3184 (2) | -3857 (4) | 50 (1) |
| C(20) | 939 (2) | -3932 (2) | -4465 (4) | 61 (1) |
| C(21) | 749 (3) | -4360 (2) | -6290 (5) | 70 (1) |
| C(22) | -315 (3) | -4035 (3) | -7479 (4) | 69 (1) |
| C(23) | -1172 (2) | -3272 (2) | -6819 (4) | 61 (1) |
| N(24) | -1003 (2) | -2859 (2) | -5034 (3) | 51 (1) |
| N(25) | -1935 (2) | -617 (2) | -5478 (4) | 68 (1) |
| C(26) | -1779 (2) | 102 (2) | -5983 (4) | 52 (1) |
| N(27) | 6875 (3) | -4018 (3) | -10973 (4) | 67 (1) |
| O(28) | 6929 (3) | -4984 (3) | -11607 (6) | 115 (2) |
| O(29) | 6153 (2) | -3570 (3) | -10109 (4) | 121 (2) |
| O(30) | 7541 (3) | -3522 (3) | -11211 (4) | 117 (2) |
| O(31) | 6205 (3) | 4035 (4) | 1011 (6) | 102 (2) |

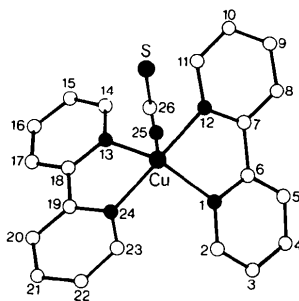


Fig. 1. The complex cation with the atom-labelling sequence used.

(Andrade, 1985). Their spectroscopic and electrochemical properties make them attractive candidates as inorganic models for metalloproteins of copper (Spiro, 1981).

Experimental. Green crystals of the title compound were prepared by the method reported by Nonoyama, Ojima, Ohki & Nonoyama (1980). Density measured by flotation using a methyl iodide-acetone mixture; crystal $0.25 \times 0.5 \times 0.05$ mm, Syntex P3 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; unit-cell parameters by least-squares fit from 4140 reflections with $3.5 \leq 2\theta \leq 55^\circ$; 5043 unique reflections measured with the ω -scan technique in the range 0 to 15, -16 to 16, -10 to 9 for h , k and l , respectively;

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

| | | | |
|-------------------|------------|-------------------|------------|
| Cu-N(1) | 2.077 (3) | Cu-N(12) | 1.989 (2) |
| Cu-N(13) | 2.080 (2) | Cu-N(24) | 1.994 (2) |
| Cu-N(25) | 2.010 (3) | S-C(26) | 1.615 (3) |
| N(1)-C(2) | 1.332 (4) | N(1)-C(6) | 1.356 (4) |
| C(2)-C(3) | 1.376 (5) | C(3)-C(4) | 1.368 (5) |
| C(4)-C(5) | 1.376 (5) | C(5)-C(6) | 1.384 (5) |
| C(6)-C(7) | 1.471 (4) | C(7)-C(8) | 1.386 (4) |
| C(7)-N(12) | 1.342 (4) | C(8)-C(9) | 1.377 (5) |
| C(9)-C(10) | 1.368 (6) | C(10)-C(11) | 1.379 (4) |
| C(11)-C(12) | 1.341 (4) | N(13)-C(14) | 1.340 (3) |
| N(13)-C(18) | 1.350 (3) | C(14)-C(15) | 1.373 (4) |
| C(15)-C(16) | 1.376 (4) | C(16)-C(17) | 1.385 (4) |
| C(17)-C(18) | 1.384 (3) | C(18)-C(19) | 1.478 (4) |
| C(19)-C(20) | 1.396 (4) | C(19)-N(24) | 1.343 (3) |
| C(20)-C(21) | 1.374 (5) | C(21)-C(22) | 1.371 (4) |
| C(22)-C(23) | 1.379 (4) | C(23)-N(24) | 1.343 (4) |
| N(25)-C(26) | 1.152 (4) | N(27)-O(28) | 1.220 (5) |
| N(27)-O(29) | 1.219 (5) | N(27)-O(30) | 1.215 (6) |
| O(31)-H(31) | 0.740 (43) | O(31)-H(32) | 0.932 (45) |
| N(1)-Cu-N(12) | 80.0 (1) | N(1)-Cu-N(13) | 119.3 (1) |
| N(12)-Cu-N(13) | 97.2 (1) | N(1)-Cu-N(24) | 99.4 (1) |
| N(12)-Cu-N(24) | 176.4 (1) | N(13)-Cu-N(24) | 80.0 (1) |
| N(1)-Cu-N(25) | 123.5 (1) | N(12)-Cu-N(25) | 91.4 (1) |
| N(13)-Cu-N(25) | 117.1 (1) | N(24)-Cu-N(25) | 91.9 (1) |
| Cu-N(1)-C(2) | 128.2 (2) | Cu-N(1)-C(6) | 113.0 (2) |
| C(2)-N(1)-C(6) | 118.4 (3) | N(1)-C(2)-C(3) | 122.7 (3) |
| C(3)-C(2)-C(6) | 119.0 (3) | C(3)-C(4)-C(5) | 119.4 (4) |
| C(4)-C(5)-C(6) | 119.0 (3) | N(1)-C(6)-C(5) | 121.4 (3) |
| N(1)-C(6)-C(7) | 114.8 (3) | C(5)-C(6)-C(7) | 123.7 (3) |
| C(6)-C(7)-C(8) | 124.2 (3) | C(6)-C(7)-N(12) | 115.2 (2) |
| C(8)-C(7)-N(12) | 120.6 (3) | C(7)-C(8)-C(9) | 120.0 (3) |
| C(8)-C(9)-C(10) | 119.3 (3) | C(9)-C(10)-C(11) | 118.4 (3) |
| C(10)-C(11)-N(12) | 122.8 (3) | Cu-N(12)-C(7) | 116.5 (2) |
| Cu-N(12)-C(11) | 124.4 (2) | C(7)-N(12)-C(11) | 119.0 (2) |
| Cu-N(13)-C(14) | 128.1 (2) | Cu-N(13)-C(18) | 113.4 (2) |
| C(14)-N(13)-C(18) | 118.4 (2) | N(13)-C(14)-C(15) | 122.9 (2) |
| C(15)-C(16)-C(17) | 118.6 (3) | C(15)-C(16)-C(17) | 119.5 (2) |
| C(16)-C(17)-C(18) | 118.8 (2) | N(13)-C(18)-C(17) | 121.7 (2) |
| N(13)-C(18)-C(19) | 114.7 (2) | C(17)-C(18)-C(19) | 123.6 (2) |
| C(18)-C(19)-C(20) | 123.6 (2) | C(18)-C(19)-N(24) | 115.4 (2) |
| C(20)-C(19)-N(24) | 121.0 (2) | C(19)-C(20)-C(21) | 119.0 (2) |
| C(20)-C(21)-C(22) | 119.6 (3) | C(21)-C(22)-C(23) | 119.2 (3) |
| C(22)-C(23)-N(24) | 121.8 (2) | Cu-N(24)-C(19) | 116.0 (2) |
| Cu-N(24)-C(23) | 124.1 (2) | C(19)-N(24)-C(23) | 119.4 (2) |
| Cu-N(25)-C(26) | 166.2 (2) | S-C(26)-N(25) | 178.7 (2) |
| O(28)-N(27)-O(29) | 119.2 (4) | O(28)-N(27)-O(30) | 119.6 (4) |
| O(29)-N(27)-O(30) | 121.3 (4) | H(31)-O(31)-H(32) | 113.9 (39) |

absorption correction ψ scan; 4140 reflections observed with $F > 3\sigma(F)$; structure solved by direct methods and refined on F by anisotropic block-diagonal-matrix least squares with program system *SHELXTL* (Sheldrick, 1985); H-atom positions calculated and considered isotropically with the exception of those corresponding to the water molecule whose positions were allowed to refine; 304 parameters varied in all, overdetermination ratio 13.5, $R = 0.041$ and $wR = 0.040$; $w^{-1} = \sigma^2(F) + 0.001F^2$; mean shift/*e.s.d.* = 0.038, max. = 0.242; final difference Fourier map excursions within -0.377 and $0.417 e \text{\AA}^{-3}$. Atomic scattering factors those of *SHELXTL*.

Discussion. The final positional and equivalent isotropic thermal parameters are listed in Table 1.* Fig. 1

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44857 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

represents the configuration of the complex cation together with the atom-labelling sequence. The central Cu^{2+} ion binds the NCS^- ion and the two bipy ligands *via* the N atoms, so that N(1), N(13) and N(25) are located in the equatorial plane of the trigonal bipyramid with the Cu^{2+} ion almost in this plane [max. deviation 0.023 (1) Å]; N(12) and N(24) occupy axial sites, with $\text{N}(12)\text{--Cu--N}(24) = 176.4 (1)^\circ$. The three equatorial N–Cu–N bond angles are close to 120° (Table 2), so that the distortion from a regular trigonal bipyramid is very small compared with the distortion found in the monoclinic $[\text{Cu}(\text{bipy})_2\text{NSC}]\text{BF}_4$ complex (Tyagi & Hathaway, 1981). In the tetrafluoroborate salt of the complex, the two Cu–N(bipy) equatorial distances are significantly different, which is not so in the present case (Table 2). There are no unusual bond lengths and bond angles in the bipy ligands. The individual pyridine rings are planar [max. deviation 0.011 (4) Å] and the pertinent dihedral angles for each bipy ligand are 5.4 and 7.1° (corresponding to 0.6 and 3.2° in the monoclinic analogous complex). The dihedral angle between the mean planes of the bipy ligands is 64.0° , which is significantly smaller than the value of 100.1° in the analogous complex. There is nothing unusual in the NCS^- ligand (Stults, Day, Marianelli & Day, 1979), but the Cu–N(25)–C(26) angle has the value of

$166.2 (2)^\circ$ compared with $174.2 (5)^\circ$ in the analogous complex.

The crystal packing is achieved with the uncoordinated nitrate ions and water molecules. There are no short intermolecular interactions that could correspond to hydrogen bonds.

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References

- ANDRADE, C. (1985). Primer Simposio de Química Inorgánica, Santiago, Chile. Abstract, p. 55–69.
 NONOYAMA, K., OJIMA, H., OHKI, K. & NONOYAMA, M. (1980). *Inorg. Chim. Acta*, **41**, 155–159.
 SHELDRIK, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Federal Republic of Germany.
 SPIRO, T. G. (1981). *Copper Proteins*, Vol. 3, chap. 4. New York: Wiley-Interscience.
 STULTS, R., DAY, R. O., MARIANELLI, R. S. & DAY, V. W. (1979). *Inorg. Chem.* **18**, 1847–1852.
 TYAGI, S. & HATHAWAY, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2029–2053.

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***cis*-Dicarbonyl-*trans*-dichloro[3,6-bis(2-pyridyl)pyridazine]ruthenium(II) (1) and *cis*-Dicarbonyl-*cis*-dichloro[3,6-bis(2-pyridyl)pyridazine]ruthenium(II) (2)**

BY G. DE MUNNO, G. DENTI AND G. DE ROSA

Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata di Rende, Cosenza, Italy

AND G. BRUNO

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Italy

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Abstract. $[\text{RuCl}_2(\text{CO})_2(\text{C}_{14}\text{H}_{10}\text{N}_4)]$. (1) $M_r = 462.3$, monoclinic, $P2_1/c$, $a = 15.004 (2)$, $b = 10.641 (1)$, $c = 10.849 (1)$ Å, $\beta = 94.31 (1)^\circ$, $V = 1727.3 (4)$ Å³, $Z = 4$, $D_x = 1.777$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 12.2$ cm⁻¹, $F(000) = 912$, $T = 298$ K, final conventional $R = 0.029$ for 2054 unique observed reflections. (2) $M_r = 462.3$, monoclinic, $P2_1/c$, $a = 7.152 (1)$, $b = 16.439 (2)$, $c = 14.708 (2)$ Å, $\beta = 93.46 (1)^\circ$, $V = 1726.0 (4)$ Å³, $Z = 4$, $D_x = 1.779$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 12.2$ cm⁻¹, $F(000) = 912$, $T = 298$ K, final conventional $R = 0.023$ for 2751 unique observed reflections. Both (1) and (2) have a six-coordinated Ru atom with a distorted

octahedral geometry, being bonded by two N atoms of the organic ligand, which acts as bidentate, by two Cl atoms and by two C atoms of CO groups. In (1) the Cl atoms are in *trans* position, the CO groups being *cis*; in (2) both Cl and CO groups are in *cis* position.

Introduction. Mono- and dinuclear ruthenium(II) complexes of chelating (Cole-Hamilton, 1980; Deacon, Patrick, Skelton, Thomas & White, 1984) and bis-chelating (Braunstein, Baker, Streckas & Gafney, 1984; Ruminski & Petersen, 1982) heterocyclic N-donor ligands are receiving much attention in view of their interesting photocatalytic properties. Among the ligands