

Comparing bond distances and angles between the two Pt(CH<sub>3</sub>)<sub>3</sub>L<sub>OR</sub> structures, nearly all agree to within experimental uncertainty. The only apparently significant differences are found in the P=O—Pt linkages: the average values for Pt—O, O—P and Pt—O—P are 2.196 (1), 1.507 (8) Å and 125.1 (9)° for Pt(CH<sub>3</sub>)<sub>3</sub>L<sub>OEt</sub>, and 2.173 (5), 1.492 (6) Å and 129.2 (3)° for the ordered molecule of Pt(CH<sub>3</sub>)<sub>3</sub>L<sub>OMe</sub>, respectively. (Values for the disordered molecule are intermediate, but the uncertainties in these parameters are considerably larger and their significance is dubious.) Increased steric crowding around the set of P=O ligands could result in a greater separation between the tripod ligand and the Pt center and the observed increase in bond lengths for Pt(CH<sub>3</sub>)<sub>3</sub>L<sub>OEt</sub>, but this interpretation predicts an increase in Pt—O—P angles, whereas a decrease is found.

The crystal structure of Pt(CH<sub>3</sub>)<sub>3</sub>L<sub>OMe</sub> exhibits an interesting feature: of the two independent molecules in the unit cell, one is disordered about a center of symmetry (Fig. 2). It may be noteworthy that each of the six C atoms of the methoxy groups virtually overlaps its partner in the other orientation of the disordered molecule; perhaps the breaking of this pseudo-symmetry element by additional substitution is responsible for the fact no such disorder was found for the ethyl analog.

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## Structures of the Nickel(II) and Copper(II) Complexes of 3-Hydroxy-6-methylpyridine-2-thione

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**Abstract.** (I) Bis(6-methylpyridine-2-thion-3-olato)-nickel(II) bis(dimethylformamide), Ni(C<sub>6</sub>H<sub>6</sub>NOS)<sub>2</sub>·2C<sub>3</sub>H<sub>7</sub>NO, *M<sub>r</sub>* = 485.28, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 8.518 (2), *b* = 13.545 (2), *c* = 9.340 (1) Å, *β* =

94.19 (2)°, *V* (241 K) = 1074.7 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>*(295 K) = 1.53 (1), *D<sub>x</sub>*(295 K); *V* = 1086.4 (3) Å<sup>3</sup> = 1.48 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 31.47 cm<sup>-1</sup>, *F*(000) = 508, *T* = 241 (1) K, *R* = 0.0500 for 1240 observed reflections. The complex is planar with the Ni ion at the origin of the unit cell. A hydrogen bond exists between the N—H of the ligand and the carbonyl O atom of the

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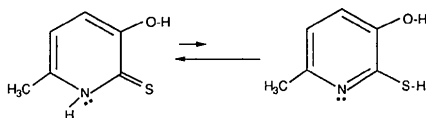
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DMF of crystallization. (II) Bis(6-methylpyridine-2-thion-3-olato)copper(II) bis(dimethylformamide),  $\text{Cu}(\text{C}_6\text{H}_6\text{NOS})_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$ ,  $M_r = 490.11$ , monoclinic,  $P2_1/c$ ,  $a = 8.599$  (2),  $b = 13.574$  (3),  $c = 9.432$  (2) Å,  $\beta = 94.33$  (2)°,  $V = 1097.8$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.55$  (1),  $D_x = 1.48$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 33.71$  cm<sup>-1</sup>,  $F(000) = 510$ ,  $T = 295$  (1) K,  $R = 0.0489$  for 805 observed reflections. This compound is isostructural with (I).

**Introduction.** The structure of 3-hydroxy-6-methylpyridine-2-thione was reported by Furberg & Schwitters (1977). Inspection of this compound indicates potential metal chelating sites between the N and the S atoms or between the S and the O atoms (see the scheme below). Furberg & Schwitters (1977) reported the structure of this ligand in the solid state to be the thione tautomer. This compound has been reported to form highly colored complexes with a number of transition metals (Contreras, 1976), without specifying the mode of complexation. We here report the structures of the nickel(II) and copper(II) complexes of this ligand as their dimethylformamide adducts.



**Experimental.** The Ni complex (I) was prepared by mixing 100 mg  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 10 mL ethanol-H<sub>2</sub>O (50:50) with 120 mg 3-hydroxy-6-methylpyridine-2-thione in 10 mL ethanol-H<sub>2</sub>O (50:50); pH = 2.8. Dilute  $\text{NH}_4\text{OH}$  was added to pH = 8.3; a brown precipitate formed. A hexagonal platelet crystal (0.55 × 0.65 × 0.80 mm, thickness 0.20 mm), from DMF-ethanol (50:50) at 295 K, was sealed in a glass capillary with a drop of mother liquor not in contact with the crystal.  $D_m$  measured by flotation. Fifteen high-angle reflections were used for the determination of the orientation matrix and cell dimensions.  $T = 241$  (1) K by blowing cold air. A Syntex  $P2_1$  diffractometer was used for data collection;  $\theta$ - $2\theta$  scan technique; fixed scan rate ( $2\theta = 2^\circ \text{ min}^{-1}$ ); graphite-monochromated  $\text{Cu } K\alpha$  radiation. Three standard reflections (324, 123, 021) monitored every 47 reflections showed  $\pm 1.92\%$  variation in intensity. 1475 unique reflections were measured;  $3 < 2\theta < 114.9^\circ$ ;  $0 \leq h \leq 9$ ,  $0 \leq k \leq 15$ ,  $-10 \leq l \leq 10$ ; 1240 reflections were considered observed [ $I \geq 3\sigma(I)$ ]. Absorption corrections based on eight crystal faces were applied ( $1.535 \leq A \leq 3.008$ , average = 1.889) (Alcock, 1970). The structure was solved using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The positions of all non-H atoms, including those in the DMF of crystallization, were found

from the best  $E$  map. All of the pyridine-ring H atoms and at least one of each of the methyl-group H atoms were found in difference maps; positions of the remaining H atoms were calculated. Non-H atoms were allowed anisotropic thermal motion in full-matrix least-squares refinement on  $F$ . H-atom positional parameters were fixed; isotropic thermal parameters at  $(B + 1) \text{ \AA}^2$  ( $B$  is the value for the atom to which the H is bound).  $\sum w||F_o| - |F_c||^2$  minimized;  $R = 0.0500$ ,  $wR = 0.0622$ ,  $S = 1.04$ ,  $w = 1/\sigma^2$  ( $\sigma = 0.057F_o - 1.418$  for  $F_o \geq 140$ ,  $\sigma = 0.006F_o + 8.300$  for  $F_o < 140$ ), last cycle maximum  $\Delta/\sigma = 0.0041$ , average = 0.0008, final  $\Delta F$  maximum = 0.91 at the S=C double bond, minimum =  $0.13 \text{ e \AA}^{-3}$ . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72-98) as well as anomalous-dispersion corrections used for the S atom and the  $\text{Ni}^{2+}$  ion (Vol. III, p. 214, Table 3.3.2B). Computer programs have been referenced previously (Lalancette, Vanderhoff & Thompson, 1990).

The Cu complex (II) was prepared by adding 39.3 mg  $\text{CuO}$  to 25 mL of 0.05N HCl-ethanol (4:1) containing 146.7 mg  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and 141.7 mg 3-hydroxy-6-methylpyridine-2-thione with constant stirring. The suspension was heated to 348 K in 15 min, then cooled to 295 K. The mixture turned from yellow to gold; on cooling, a whitish gray precipitate and greenish gold solution formed. The filtered solution was made basic by dropwise addition of dilute  $\text{NH}_4\text{OH}$ ; a brown precipitate formed. A parallelepiped crystal ( $0.075 \times 0.075 \times 0.44$  mm), from DMF-ethanol (50:50), was sealed in a capillary in the presence of mother liquor as for (I). Data were collected as for complex (I) except:  $T = 295$  (1) K; three standard reflections (111, 122,  $31 \bar{3}$ ) monitored every 27 reflections showed  $\pm 0.79\%$  intensity variation; 1130 unique reflections measured;  $3 < 2\theta < 100.0^\circ$ ;  $0 \leq h \leq 9$ ,  $0 \leq k \leq 13$ ,  $-9 \leq l \leq 9$ ; 805 reflection considered observed [ $I \geq 3\sigma(I)$ ]; absorption corrections based on six crystal faces ( $1.130 \leq A \leq 1.348$ , average = 1.186). Since (II) was apparently isostructural with (I) (with essentially the same density, cell dimensions and space group), atomic parameters for non-H atoms from (I) were used as initial parameters for the refinement of (II) ( $R = 0.16$ ). All of the pyridine-ring H atoms and at least one of each of the methyl-group H atoms were found in difference Fourier maps; remaining H-atom positions were calculated; all were given isotropic thermal parameters as above. Non-H atoms were refined with anisotropic thermal parameters. H-atom parameters were held fixed.  $\sum w||F_o| - |F_c||^2$  minimized;  $R = 0.0489$ ,  $wR = 0.0582$ ,  $S = 1.15$ ,  $w = 1/\sigma^2$  ( $\sigma = 0.118F_o - 17.400$  for  $F_o \geq 230$ ,  $\sigma = 0.038F_o + 1.100$  for  $57 \leq F_o < 230$ , and  $\sigma = -0.044F_o + 6.000$  for  $F_o < 57$ ), last cycle maximum  $\Delta/\sigma = 0.0046$ , aver-

Table 1. Fractional atomic coordinates and isotropic thermal parameters (Å<sup>2</sup>) for compounds (I) and (II)
$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

| Compound (I) | x          | y           | z          | B <sub>eq</sub> |
|--------------|------------|-------------|------------|-----------------|
| Ni           | 0.0        | 0.0         | 0.0        | 2.20 (1)        |
| S(1)         | 0.8440 (1) | 0.06679 (7) | 0.1514 (1) | 2.55 (1)        |
| O(1)         | 1.0336 (3) | -0.1069 (2) | 0.1228 (3) | 2.53 (1)        |
| O(2)         | 0.6347 (3) | 0.1463 (2)  | 0.4764 (3) | 3.33 (1)        |
| N(1)         | 0.8086 (4) | -0.0209 (2) | 0.4070 (3) | 2.13 (1)        |
| N(2)         | 0.5499 (4) | 0.3019 (2)  | 0.4239 (4) | 2.61 (1)        |
| C(1)         | 0.8726 (4) | -0.0239 (3) | 0.2789 (4) | 2.10 (2)        |
| C(2)         | 0.9690 (4) | -0.1056 (3) | 0.2475 (4) | 2.21 (2)        |
| C(3)         | 0.9909 (5) | -0.1785 (3) | 0.3495 (4) | 2.62 (2)        |
| C(4)         | 0.9198 (5) | -0.1721 (3) | 0.4794 (4) | 2.63 (2)        |
| C(5)         | 0.8290 (4) | -0.0928 (3) | 0.5090 (4) | 2.27 (2)        |
| C(6)         | 0.7458 (5) | -0.0794 (3) | 0.6440 (4) | 2.96 (2)        |
| C(7)         | 0.6377 (5) | 0.2231 (3)  | 0.4064 (5) | 2.90 (2)        |
| C(8)         | 0.5635 (6) | 0.3901 (4)  | 0.3365 (5) | 3.78 (2)        |
| C(9)         | 0.4437 (6) | 0.3075 (4)  | 0.5386 (6) | 3.99 (2)        |

| Compound (II) | x           | y           | z           | B <sub>eq</sub> |
|---------------|-------------|-------------|-------------|-----------------|
| Cu            | 0.0         | 0.0         | 0.0         | 3.01 (1)        |
| S(1)          | 0.8378 (2)  | 0.0676 (1)  | 0.1557 (2)  | 3.58 (1)        |
| O(1)          | 1.0309 (5)  | -0.1091 (3) | 0.1263 (4)  | 3.42 (2)        |
| O(2)          | 0.6339 (5)  | 0.1458 (4)  | 0.4788 (5)  | 4.48 (2)        |
| N(1)          | 0.8075 (6)  | -0.0206 (3) | 0.4064 (5)  | 2.95 (2)        |
| N(2)          | 0.5490 (6)  | 0.3017 (4)  | 0.4251 (6)  | 3.43 (3)        |
| C(1)          | 0.8703 (7)  | -0.0247 (4) | 0.2787 (6)  | 2.67 (3)        |
| C(2)          | 0.9656 (7)  | -0.1052 (4) | 0.2500 (7)  | 2.80 (3)        |
| C(3)          | 0.9889 (7)  | -0.1768 (4) | 0.3539 (7)  | 3.40 (3)        |
| C(4)          | 0.9186 (8)  | -0.1705 (5) | 0.4818 (7)  | 3.63 (3)        |
| C(5)          | 0.8287 (7)  | -0.0906 (5) | 0.5095 (7)  | 3.24 (3)        |
| C(6)          | 0.7464 (8)  | -0.0773 (5) | 0.6435 (7)  | 3.98 (3)        |
| C(7)          | 0.6364 (8)  | 0.2227 (6)  | 0.4089 (7)  | 3.94 (4)        |
| C(8)          | 0.5635 (10) | 0.3889 (6)  | 0.3363 (9)  | 5.22 (4)        |
| C(9)          | 0.4408 (9)  | 0.3060 (6)  | 0.5361 (10) | 5.86 (4)        |

Table 2. Bond distances (Å) for compounds (I) and (II)

|              | Compound (I)<br>(M = Ni) | Compound (II)<br>(M = Cu) |
|--------------|--------------------------|---------------------------|
| M—S(1)       | 2.204 (1)                | 2.292 (2)                 |
| M—O(1)       | 1.856 (3)                | 1.906 (4)                 |
| S(1)—C(1)    | 1.716 (4)                | 1.716 (6)                 |
| N(1)—C(1)    | 1.351 (5)                | 1.358 (8)                 |
| C(1)—C(2)    | 1.421 (6)                | 1.404 (9)                 |
| O(1)—C(2)    | 1.325 (5)                | 1.334 (7)                 |
| C(2)—C(3)    | 1.375 (6)                | 1.385 (8)                 |
| C(3)—C(4)    | 1.398 (6)                | 1.392 (9)                 |
| C(4)—C(5)    | 1.364 (6)                | 1.369 (9)                 |
| N(1)—C(5)    | 1.365 (5)                | 1.362 (8)                 |
| C(5)—C(6)    | 1.502 (6)                | 1.505 (9)                 |
| O(2)—C(7)    | 1.230 (5)                | 1.235 (9)                 |
| N(2)—C(7)    | 1.321 (5)                | 1.325 (9)                 |
| N(2)—C(8)    | 1.456 (6)                | 1.462 (9)                 |
| N(2)—C(9)    | 1.454 (6)                | 1.453 (9)                 |
| N(1)—H(N1)   | 0.956                    | 0.969                     |
| C(3)—H(C3)   | 0.988                    | 0.952                     |
| C(4)—H(C4)   | 0.945                    | 0.955                     |
| C(6)—H(C6)   | 0.948                    | 0.934                     |
| C(6)—H'(C6)  | 0.945                    | 0.944                     |
| C(6)—H''(C6) | 0.950                    | 0.957                     |
| C(7)—H(C7)   | 0.996                    | 0.932                     |
| C(8)—H(C8)   | 0.936                    | 0.924                     |
| C(8)—H'(C8)  | 0.934                    | 0.956                     |
| C(8)—H''(C8) | 0.916                    | 0.959                     |
| C(9)—H(C9)   | 0.946                    | 0.924                     |
| C(9)—H'(C9)  | 0.905                    | 0.950                     |
| C(9)—H''(C9) | 0.955                    | 0.963                     |

Table 3. Bond angles (°) for compounds (I) and (II)

|                     | Compound (I)<br>(M = Ni) | Compound (II)<br>(M = Cu) |
|---------------------|--------------------------|---------------------------|
| S(1)—M—O(1)         | 89.8 (1)                 | 88.5 (1)                  |
| S(1)—M—O(1')*       | 90.2 (1)                 | 91.5 (1)                  |
| M—S(1)—C(1)         | 95.1 (1)                 | 93.7 (2)                  |
| M—O(1)—C(2)         | 118.5 (2)                | 117.9 (4)                 |
| C(1)—N(1)—C(5)      | 123.9 (3)                | 124.3 (5)                 |
| C(1)—N(1)—H(N1)     | 118.0                    | 118.1                     |
| C(5)—N(1)—H(N1)     | 118.1                    | 117.5                     |
| C(7)—N(2)—C(8)      | 121.6 (4)                | 121.0 (6)                 |
| C(7)—N(2)—C(9)      | 121.5 (4)                | 121.0 (6)                 |
| C(8)—N(2)—C(9)      | 116.7 (3)                | 117.9 (6)                 |
| S(1)—C(1)—N(1)      | 123.2 (3)                | 120.9 (4)                 |
| S(1)—C(1)—C(2)      | 118.0 (3)                | 120.4 (5)                 |
| N(1)—C(1)—C(2)      | 118.8 (3)                | 118.7 (5)                 |
| O(1)—C(2)—C(1)      | 118.4 (3)                | 119.3 (5)                 |
| O(1)—C(2)—C(3)      | 123.7 (3)                | 122.9 (5)                 |
| C(1)—C(2)—C(3)      | 117.9 (4)                | 117.8 (6)                 |
| C(2)—C(3)—C(4)      | 120.7 (4)                | 121.4 (6)                 |
| C(2)—C(3)—H(C3)     | 119.3                    | 119.1                     |
| C(4)—C(3)—H(C3)     | 120.0                    | 119.5                     |
| C(3)—C(4)—C(5)      | 120.9 (4)                | 120.2 (6)                 |
| C(3)—C(4)—H(C4)     | 119.3                    | 119.7                     |
| C(5)—C(4)—H(C4)     | 119.8                    | 120.2                     |
| N(1)—C(5)—C(6)      | 117.7 (4)                | 117.6 (6)                 |
| N(1)—C(5)—C(6)      | 117.1 (3)                | 118.0 (6)                 |
| C(4)—C(5)—C(6)      | 125.1 (4)                | 124.3 (6)                 |
| C(5)—C(6)—H(C6)     | 108.9                    | 110.6                     |
| C(5)—C(6)—H'(C6)    | 109.4                    | 111.9                     |
| C(5)—C(6)—H''(C6)   | 109.2                    | 108.4                     |
| H(C6)—C(6)—H'(C6)   | 109.4                    | 112.1                     |
| H(C6)—C(6)—H''(C6)  | 108.9                    | 100.5                     |
| H'(C6)—C(6)—H''(C6) | 111.0                    | 112.8                     |
| O(2)—C(7)—N(2)      | 125.7 (4)                | 126.1 (6)                 |
| O(2)—C(7)—H(C7)     | 124.2                    | 124.0                     |
| N(2)—C(7)—H(C7)     | 110.1                    | 109.6                     |
| N(2)—C(8)—H(C8)     | 104.9                    | 107.5                     |
| N(2)—C(8)—H'(C8)    | 108.0                    | 108.8                     |
| N(2)—C(8)—H''(C8)   | 102.5                    | 108.8                     |
| H(C8)—C(8)—H'(C8)   | 103.8                    | 107.8                     |
| H(C8)—C(8)—H''(C8)  | 123.7                    | 107.4                     |
| H'(C8)—C(8)—H''(C8) | 112.9                    | 116.3                     |
| N(2)—C(9)—H(C9)     | 109.6                    | 108.8                     |
| N(2)—C(9)—H'(C9)    | 112.7                    | 109.4                     |
| N(2)—C(9)—H''(C9)   | 109.1                    | 108.8                     |
| H(C9)—C(9)—H'(C9)   | 109.9                    | 110.8                     |
| H(C9)—C(9)—H''(C9)  | 106.2                    | 109.6                     |
| H'(C9)—C(9)—H''(C9) | 109.2                    | 109.5                     |

\* Atom O(1') generated through symmetry (2 - x, -y, -z).

age = 0.0010, final  $\Delta F$  maximum = 0.85 at the S=C double bond, minimum = 0.08 e Å<sup>-3</sup>. Source of atomic scattering factors as above; anomalous-dispersion corrections used for the S atom and for the Cu<sup>2+</sup> ion.

**Discussion.** The Ni<sup>2+</sup> ion in (I) and the Cu<sup>2+</sup> ion in (II) sit at the origin of the cell, with one of the two complexing ligands and one of the two DMF molecules of crystallization comprising the asymmetric unit. These structures, (I) and (II), are isostructural. Table 1 lists positional and isotropic thermal parameters\* for (I) and (II). Table 2 is a comparison of the bond distances for (I) and (II), and Table 3 is a comparison of the bond angles. Fig. 1 presents a view of (I) and/or (II), with the numbering scheme of the asymmetric unit. Because the ligand is known to be the thione tautomer (Furberg & Schwitters, 1977), there are two possible chelating sites: between the S and the O atom (loss of the O—H proton), or

\* Lists of H-atom positional and isotropic thermal parameters, anisotropic thermal parameters for the other atoms, and structure factors for complexes (I) and (II), as well as the positional and thermal parameters for 3-hydroxy-6-methylpyridine-2-thione as obtained in our laboratory have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54981 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

between the N and the S atom (loss of the N—H proton). The structures of the metal complexes (I) and (II) reveal that the chelation occurs between the S and O atoms of the ligand, and the metal ion. Fig. 2 is a partial packing diagram showing the relationship between the complex and the DMF molecules of crystallization. The complexes are almost planar, with a dihedral angle between the pyridine ring system [C(1), C(3) and C(5)] and the ring formed upon chelation [ $M$ , C(1) and O(1)] of  $2.6 (1)^\circ$  in (I) and  $4.2 (2)^\circ$  in (II). The H atom bound to the

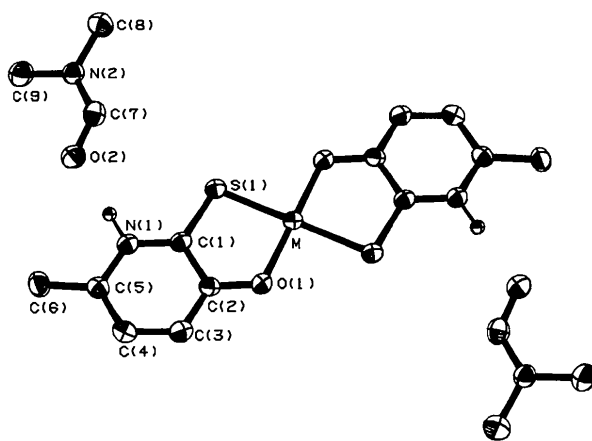


Fig. 1. A view of the metal-ligand complex (50% probability ellipsoids). The numbering scheme of the asymmetric unit is shown with  $M = \text{Ni}^{\text{II}}$  for compound (I),  $M = \text{Cu}^{\text{II}}$  for compound (II). The hydrogen bond between the ligand and the DMF of crystallization is apparent.

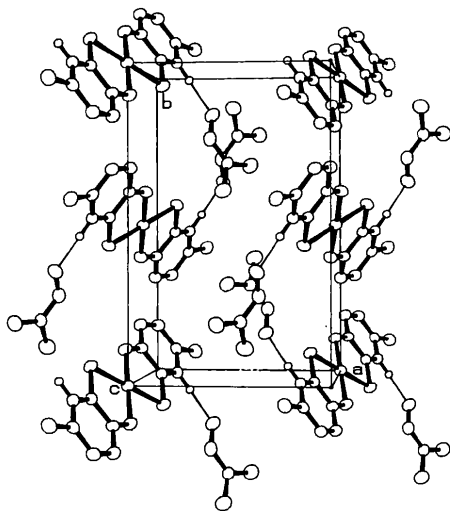


Fig. 2. A partial packing diagram for (I) and/or (II) showing the relationships between the metal-ligand complex and the DMF molecules of crystallization.

N atom of the ligand was found by difference Fourier, and not refined. A hydrogen bond exists between the carbonyl O atom of the DMF of crystallization and the N atom of the ligand [ $\text{N}\cdots\text{O}$  2.808 (4) Å for (I) and 2.820 (7) Å for (II)];  $\text{N}\cdots\text{O}$  hydrogen bonds are in the range 2.73–3.22 Å [*International Tables for X-ray Crystallography* (1974, Vol. III, p. 273, Table 4.1.12)]. In (I), the observed Ni—O bond length of 1.856 (3) Å is longer than the 1.815–1.846 Å Ni—O bond lengths reported for various square planar complexes (Kamenar, Kaitner, Stefanović & Waters, 1990); the Ni—S bond length of 2.204 (1) Å is at the upper limit of the reported values of 2.139–2.204 Å (Gyepes & Głowiak, 1989; Srdanov, Jacobson & Wudl, 1990). In (II), the observed Cu—O bond length of 1.906 (4) Å is within the reported range for square planar complexes [1.878–1.97 Å] (Fawcett, Ushay, Rose, Lalancette, Potenza & Schugar, 1979; Castiñeiras, Hiller, Strähle, Romero, Bastida & Sousa, 1990); the Cu—S length of 2.292 (2) Å is at the upper limit of the reported bond lengths of 2.269–2.292 Å (Schugar, Ou, Thich, Potenza, Felthouse, Haddad, Hendrickson, Furey & Lalancette, 1980). The bond lengths in structures (I) and (II) are typical even though these complexes have slightly distorted square planes [ $\text{O—S—O}'$  angle of  $80.20 (8)^\circ$  and  $\text{S—O—S}'$  angle of  $99.80 (8)^\circ$  for (I); and  $\text{O—S—O}'$  angle of  $79.5 (1)^\circ$  and  $\text{S—O—S}'$  angle of  $100.5 (1)^\circ$  for (II)].

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