# Bivalent Metal Complexes of 1,11-Diamino-3,6,9-trithiaundecane and the Crystal Structures of Adducts with Nickel(II) and Copper(II) Bromides

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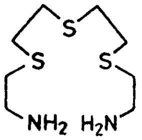
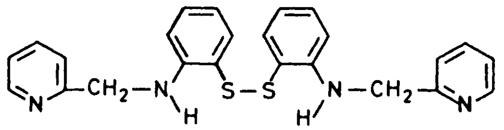
The hydrobromide salt of the quinquedentate ligand 1,11-diamino-3,6,9-trithiaundecane (L$^1$) reacts with copper(II) and nickel(II) acetates to form [MBrL$^1$]Br (M = Cu or Ni). By anion-exchange reactions a whole series of compounds of general formula [MXL$^1$]X′, X = Cl, Br, I, or NCS, X′ = Cl, Br, I, NCS, PF$_6$, or ClO$_4$, were prepared. Results of conductivity and spectroscopic measurements indicate that these species all contain six-co-ordinate metal ions. For two compounds the geometry was confirmed by *X*-ray crystallography. Crystals of [CuBrL$^1$]Br·H$_2$O are monoclinic, space group $P2_1/m$, $Z = 2$, $a = 5.559(7)$, $b = 10.009(11)$, $c = 14.720(13)$ Å, and $\beta = 90.0(1)°$. Crystals of [NiBrL$^1$]Br are orthorhombic, space group $Pmnb$, $Z = 4$, $a = 10.185(12)$, $b = 16.963(12)$, and $c = 9.028(7)$ Å. 843 and 968 Independent reflections above background have been collected on a diffractometer and refined to $R$ 0.102, 0.067 respectively for M = Cu, Ni. Both structures contain discrete cations of formula [MBrL$^1$]$^+$ which have crystallographically imposed $C_s$ symmetry. The metal atoms are in distorted octahedral environments with bond lengths [M = Cu: M–N 2.03(2), M–S 2.340(6), 2.576(9), M–Br 3.130(5)] and [M = Ni: M–N 2.074(17), M–S 2.393(6), 2.437(8), M–Br 2.578(5)]. The Cu–Br and the longer of the Cu–S bonds are mutually *trans* and are particularly long due to the Jahn–Teller effect.

As part of a study into sulphur–nitrogen chelating ligands we have prepared the quinquedentate ligand 1,11-diamino-3,6,9-trithiaundecane (L$^1$) and investigated its reactions with a number of bivalent metal ions concentrating upon the species formed by nickel(II) and copper(II). The metal complexes formed by sulphur–nitrogen chelating agents have been reviewed.[1] While many such compounds are known, the only three quinquedentate ligands of the nitrogen–sulphur class that have been studied with nickel(II) and copper(II) of which we are aware are bis[2-(2-pyridylmethylamino)phenyl] disulphide (L$^2$),[2,3] the related bis[2-(2-pyridylmethylamino)ethyl] disulphide (L$^3$),[4,5] and the macrocycle 2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene (L$^4$).[6] The first two ligands contain six donor atoms but in the complexes formed by nickel(II) with L$^2$ it was suggested on the evidence provided by spectroscopic and conductance measurements that only one sulphur atom in the disulphide unit was co-ordinated to the metal.[2] This suggestion was later confirmed by *X*-ray crystallography.[3] Seff and co-workers [3] have studied the structures of a number of metal complexes formed by L$^3$ and in [NiXL$^3$][ClO$_4$] (X = Br or Cl) an identical co-ordination mode was observed to that seen in [NiClL$^2$]-[ClO$_4$]. The quinquedentate 17-membered macrocycle L$^4$ gives rise to many complexes of different types but relevant here is the crystal structure of [CuL$^4$]$^{2+}$.[6]

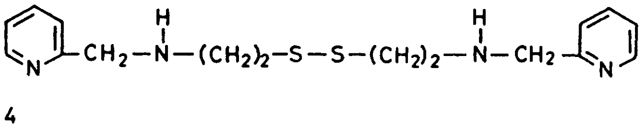
L$^1$



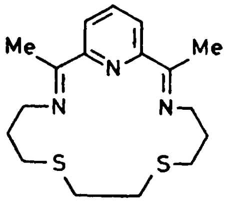
L$^2$



L$^3$



L$^4$



We now report single-crystal *X*-ray investigations into two compounds formed by L$^1$ namely [NiBrL$^1$]Br and [CuBrL$^1$]Br and spectroscopic details of some related compounds.

## EXPERIMENTAL

*Physical Measurements.*—Infrared spectra were obtained from Nujol mulls or KBr discs using a P.E. 577 spectrophotometer. Ultraviolet–visible spectra were obtained with a Beckmann Acta MIV fitted with a reflectance sphere for measurements on solids. Magnetic properties were examined by Faraday and Gouy techniques.

*Preparation of* 1,11-*Diamino*-3,6,9-*trithiaundecane* (L$^1$).—The thiol S(CH$_2$CH$_2$SH)$_2$ (10 g) was added to a solution of sodium in dry ethanol (5.8 g in 120 cm$^3$) under an atmosphere of dry nitrogen. The reaction mixture was vigorously stirred and gently heated in a three-necked flask fitted with condenser and silica gel drying tube. After 0.25 h 2-bromoethylamine hydrobromide (26 g) was added and the resulting mixture heated under reflux for 4 h. After allowing the mixture to cool overnight, the precipitated sodium bromide was removed by filtration. The solvent was removed under reduced pressure and the crude ligand isolated as a white solid. The product was recrystallised from HBr–ethanol solution, and $L^1\cdot 2HBr$ so obtained in 83% yield (Found: C, 23.2; H, 4.9; N, 6.5. Calc. for $C_8H_{22}Br_2N_2S_3$: C, 23.8; H, 5.4; N, 6.9%).

*Preparation of the Complexes formed by* $L^1$ *with* $Cu^{II}$ *and* $Ni^{II}$.—The bivalent metal acetate (2 mmol) and an equimolar amount of $L^1\cdot 2HBr$ were heated under reflux in methanol (75 cm$^3$) for 3 h. The solution was allowed to cool and the product formed as a crystalline precipitate. The product was recrystallised from ethanol, filtered off, and dried *in vacuo*.

Anion-exchange reactions were performed by warming the bromide with an appropriate salt in methanolic solution (KI, Li[NCS], Na[ClO$_4$], or Na[PF$_6$]).

*Structural Determination*.—Recrystallisation of the copper(II) bromide and nickel(II) bromide complexes yielded crystals suitable for single-crystal *X*-ray studies.

*Crystal data*. (1) $[CuBrL^1]Br\cdot H_2O$, $C_8H_{22}Br_2CuN_2OS_3$, $M = 481.7$, Monoclinic, $a = 5.559(7)$, $b = 10.009(11)$, $c = 14.720(13)$ Å, $\beta = 90.0(1)°$, $U = 819.02$ Å$^3$, $D_m = 1.96(1)$, $Z = 2$, $D_c = 1.95$ g cm$^{-3}$, $F(000) = 478$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 69.2$ cm$^{-1}$, space group $P2_1/m$ from systematic absences $0k0$, $k = 2n + 1$ and the successful structure determination.

(2) $[NiBrL^1]Br$, $C_8H_{20}Br_2N_2NiS_3$, $M = 458.5$, Orthorhombic, $a = 10.185(12)$, $b = 16.963(12)$, $c = 9.028(7)$ Å, $U = 1\,559.8$ Å$^3$, $D_m = 1.94(1)$, $Z = 4$, $D_c = 1.95(1)$ g cm$^{-3}$, $F(000) = 912$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 69.6$ cm$^{-1}$, space group *Pmnb* (No. 62) from systematic absences $h0l$, $h + l = 2n + 1$, $hk0$, $k = 2n + 1$, and the successful structure determination. Both crystals [dimensions (1) 1.5 × 0.2 × 0.6 mm; (2) 0.8 × 0.1 × 0.3 mm] were mounted with $a^*$ (1), $a$ (2) parallel to the instrument axis of a GE XRD5 diffractometer which was used to measure intensities by the stationary-crystal-stationary-counter method (counting time of 10 s). The instrument was equipped with a manual goniostat, scintillation counter, and pulse height discriminator. Backgrounds were obtained from plots of background counts against 2θ. Several standard reflections monitored during the course of the experiments showed no significant changes throughout the experimental period. For (1) 1 126 and (2) 1 158 independent reflections were measured with $2\theta < 45°$ (1), $< 50°$ (2) of which 843 [for (1)] and 968 [for (2)] with $I > 2\sigma(I)$ were employed in the subsequent calculations. Absorption corrections were applied but no extinction corrections.

TABLE 1

Atomic co-ordinates (× 10$^4$) with estimated standard deviations in parentheses for M = Cu

| Atom | *X* | *Y* | *Z* |
|---|---|---|---|
| Cu(1) | 7 281(6) | 2 500(0) | 3 120(3) |
| Br(1) | 3 836(6) | 2 500(0) | 4 802(2) |
| Br(2) | 8 326(6) | 2 500(0) | 8 423(3) |
| N(1) | 8 803(32) | 4 001(17) | 3 849(13) |
| C(2) | 8 945(42) | 5 275(22) | 3 341(16) |
| C(3) | 6 487(37) | 5 605(23) | 2 980(16) |
| S(4) | 4 999(9) | 4 195(6) | 2 444(4) |
| C(5) | 5 930(49) | 4 264(25) | 1 235(19) |
| C(6) | 8 545(41) | 3 914(22) | 1 061(16) |
| S(7) | 9 834(14) | 2 500(0) | 1 660(6) |
| O(1) | 3 393(41) | 2 500(0) | 9 598(19) |

*Solution and refinement*. Both structures were solved by Patterson methods and successive Fourier maps were then calculated to determine the remaining non-hydrogen atom positions. All the hydrogen atoms were placed in tetrahedral positions at bonding distances from the carbon and nitrogen atoms. In the least-squares refinements all atoms (bar hydrogen) were given anisotropic thermal parameters. The hydrogen atoms were given isotropic thermal parameters which were fixed for M = Cu, but allowed to refine for M = Ni although values for hydrogen atoms bonded to the same atom were constrained to be equivalent. Refinement by full-matrix least squares gave *R* values of 0.102 and 0.067 for (1) and (2) respectively. The weighting scheme employed was of the type $\sqrt{w} = 1$ for $F_o < F^*$ and $F^*/F_o$ for $F_o > F^*$. Values of 50 and 100 respectively for $F^*$ gave approximately constant values of $w\Delta^2$ over the ranges of $F_o$ and $(\sin\theta)/\lambda$. Calculations were made using the 'Shelx '76' system of programs [7] at the University of Manchester Computer Centre while scattering factors were obtained from ref. 8. In the last cycles of refinement shifts were less than 0.2σ; the final difference-Fourier map showed no significant peaks and the zero-weighted unobserved reflections revealed no serious discrepancies.

TABLE 2

Atomic co-ordinates (× 10$^4$) with estimated standard deviations in parentheses for M = Ni

| Atom | *X* | *Y* | *Z* |
|---|---|---|---|
| Ni | 2 500(0) | 3 325(2) | 1 175(4) |
| Br(1) | 2 500(0) | 1 833(2) | 639(4) |
| Br(2) | 2 500(0) | 4 821(2) | 7 335(4) |
| N(1) | 4 000(16) | 3 479(10) | −351(19) |
| C(2) | 5 269(20) | 3 703(14) | 271(27) |
| C(3) | 5 586(22) | 3 192(15) | 1 664(25) |
| S(4) | 4 232(5) | 3 131(3) | 2 929(6) |
| C(5) | 4 288(25) | 4 053(13) | 3 954(24) |
| C(6) | 3 914(21) | 4 791(14) | 3 131(28) |
| S(7) | 2 500(0) | 4 709(4) | 1 898(9) |

Positional co-ordinates are listed in Tables 1 and 2, ligand torsion angles in Table 3, and bond lengths and angles in Table 4. Structure factor tables, hydrogen-atom positions, and anisotropic thermal parameters are in Supplementary Publication No. SUP 22888 (15 pp.).*

TABLE 3

Torsion angles (°) *

| | M = Cu | M = Ni |
|---|---|---|
| M–N(1)–C(2)–C(3) | 52.7 | 44.6 |
| N(1)–C(2)–C(3)–S(4) | −46.3 | −47.4 |
| C(2)–C(3)–S(4)–C(5) | −89.4 | −79.8 |
| C(3)–S(4)–C(5)–C(6) | 70.4 | 70.9 |
| S(4)–C(5)–C(6)–S(7) | 42.8 | 41.4 |
| C(5)–C(6)–S(7)–C(6$^{I}$) | 75.2 | 80.4 |

* In the two structures the superscripts refer to the following equivalent positions.

| M = Cu | M = Ni |
|---|---|
| (I) $x, \frac{1}{2} - y, z$ | (I) $\frac{1}{2} - x, y, z$ |
| (II) $-1 + x, y, z$ | (II) $x, y, -1 + z$ |
| (III) $1 + x, y, z$ | |

RESULTS AND DISCUSSION

The quinquedentate ligand $NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2$ ($L^1$) was allowed to react with the bivalent acetates of cobalt, nickel, and copper. With the exception of cobalt, all the compounds isolated had analyses consistent with a simple stoicheiometry (Table

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

5). With cobalt(II) acetate non-stoicheiometric products were obtained that appeared to contain some cobalt(III). Attempts were made to prevent partial oxidation but these were unsuccessful. Although all the products were recrystallised, crystals of only two species [NiBrL$^1$]Br and [CuBrL$^1$]Br·$H_2O$ proved suitable for single-crystal *X*-ray crystallographic studies. Powder photographs showed that none of the compounds listed in Table 5 is isomorphous with any other in the Table. The two compounds available for detailed study, [NiBrL$^1$]Br and [CuBrL$^1$]Br·$H_2O$, differ only in the nature of the metal atom and thus provide an excellent pair for the study of the Jahn–Teller distortion that is seen with $d^9$ ions.

TABLE 4

Molecular dimensions; bond lengths (Å) and angles (°)

| | M = Cu | M = Ni |
|---|---|---|
| M–N(1) | 2.03(2) | 2.074(17) |
| M–S(4) | 2.340(6) | 2.393(6) |
| M–S(7) | 2.576(9) | 2.437(8) |
| M–Br(1) | 3.130(5) | 2.578(5) |
| N(1)–M–S(4) | 85.1(5) | 85.1(5) |
| N(1)–M–S(7) | 102.2(5) | 93.2(5) |
| N(1)–M–Br(1) | 80.6(5) | 89.9(5) |
| N(1)–M–S($4^I$) | 170.6(5) | 179.3(5) |
| N(1)–M–N($1^I$) | 95.4(5) | 94.9(7) |
| S(4)–M–S(7) | 86.8(2) | 87.4(2) |
| S(4)–M–Br(1) | 90.3(2) | 89.4(2) |
| S(4)–M–S($4^I$) | 92.9(2) | 95.0(2) |
| S(7)–M–Br(1) | 175.7(2) | 175.3(3) |
| N(1)–C(2) | 1.48(3) | 1.64(3) |
| C(2)–C(3) | 1.50(3) | 1.56(3) |
| C(3)–S(4) | 1.82(2) | 1.79(2) |
| S(4)–C(5) | 1.85(3) | 1.82(2) |
| C(5)–C(6) | 1.52(3) | 1.50(3) |
| C(6)–S(7) | 1.81(2) | 1.83(2) |
| M–N(1)–C(2) | 113.1(14) | 115.4(14) |
| N(1)–C(2)–C(3) | 108.6(18) | 110.4(18) |
| C(2)–C(3)–S(4) | 113.4(16) | 112.7(15) |
| M–S(4)–C(5) | 106.5(8) | 104.0(8) |
| C(3)–S(4)–C(5) | 105.1(11) | 104.5(11) |
| M–S(4)–C(3) | 97.6(7) | 97.9(8) |
| S(4)–C(5)–C(6) | 114.9(18) | 117.2(16) |
| C(5)–S(6)–S(7) | 118.5(17) | 115.9(17) |
| M–S(7)–C(6) | 100.8(8) | 103.7(8) |
| C(6)–S(7)–C($6^I$) | 102.5(8) | 104.2(11) |

TABLE 5

Analytical data

| | | Found (%) | | | | Required (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| Complex | Colour | C | H | N | M | C | H | N | M |
| [NiBrL$^1$]Br | Bright purple | 21.0 | 4.5 | 5.9 | 12.6 | 20.9 | 4.3 | 6.1 | 12.8 |
| [NiIL$^1$]I | Purple-brown | 17.6 | 3.6 | 5.0 | 10.6 | 17.4 | 3.6 | 5.1 | 10.6 |
| [Ni(NCS)L$^1$][NCS] | Pale purple | 27.4 | 4.9 | 12.5 | 14.1 | 27.7 | 5.1 | 12.9 | 14.1 |
| [NiBrL$^1$][$ClO_4$] | Pale purple | 20.3 | 4.2 | 5.8 | 12.0 | 20.1 | 4.2 | 5.9 | 12.3 |
| [NiBrL$^1$][$PF_6$] | Pale purple | 18.2 | 3.9 | 5.3 | 11.1 | 18.3 | 3.8 | 5.3 | 11.2 |
| [CuBrL$^1$]Br | Dark green | 20.6 | 4.1 | 5.7 | 13.7 | 20.6 | 4.3 | 6.0 | 13.7 |
| | | | | | | 19.9 | 4.7 | 5.8 | 13.2 * |
| [CuIL$^1$]I | Dark purple | 16.2 | 3.8 | 4.4 | 11.0 | 16.6 | 3.8 | 4.8 | 11.0 |
| [Cu(NCS)L$^1$][NCS] | Bright green | 26.6 | 4.7 | 13.1 | 14.3 | 28.6 | 4.8 | 13.3 | 15.1 |
| [CuBrL$^1$][$ClO_4$] | Pale grey-green | 20.3 | 4.6 | 5.6 | 12.6 | 19.9 | 4.1 | 5.8 | 13.1 |
| [CuBrL$^1$][$PF_6$] | Dark green | 17.1 | 3.9 | 5.2 | 11.3 | 17.6 | 4.0 | 5.1 | 11.6 |

* Calculated for [CuBrL$^1$]Br·$H_2O$.

The unit cells of [CuBrL$^1$]Br·$H_2O$ and [NiBrL$^1$]Br are shown in Figures 1 and 2 in the *a* and *c* projections respectively. Both cations contain the metal ion in a six-co-ordinate environment. Although the structures belong to different space groups both discrete [MBrL$^1$]$^+$ cations have crystallographic imposed $C_s$ symmetry with M, Br(1), and S(7) sitting on the mirror plane. The bromide anions [Br(2)] are also on these mirror planes. In the copper structure one molecule of water per cation was detected in the lattice. Whether this water was incorporated during the recrystallisation or was present in the first product we are unable to say. Although the analytical figures obtained for the first product agree well with those expected, as can be seen from Table 5, the presence of one molecule of water causes only a small change in the expected analytical figures.

From the torsion angles (Table 3) it is apparent that the ligand conformation in both cations is the same, therefore the differences between the two structures are most clearly seen by an examination of the bond lengths and angles (Table 4). The metal ions crystal radii are estimated at 0.87 Å and 0.83 Å for copper(II) and nickel(II) respectively,[9] thus slightly longer distances are to be expected in the copper ion and indeed the four M–N(1) and M–S(4) bonds are longer for M = Cu than M = Ni by approximately this amount. However the mutually *trans* M–S(7) bonds [2.576(9) Å M = Cu, 2.437(8) Å M = Ni] and M–Br(1) bonds [3.130(5) Å M = Cu, 2.578(5) Å M = Ni] differ by much more in the two structures, and this is attributable to an elongation of the pseudo-octahedral co-ordination sphere in the copper ion.

The copper–sulphur distances are comparable to those observed for the six-co-ordinate copper atom found in bis[3,4-bis(2-aminoethylthio)toluene]-μ-chloro-chloro-dicopper(II) diperchlorate [10] in which the co-ordination sphere consists of two nitrogen, two sulphur, and two chlorine atoms. There is a long copper–sulphur distance [2.609(6) Å] directly analogous to the long copper–sulphur bond in the present structure. In both species these long copper–sulphur bonds are *trans* to very long copper–halogen bonds. The short or equatorial copper–sulphur distance in the present structure [2.34(1) Å] is similar to a whole range of copper–sulphur distances,[11] and in particular those in the octahedral species [Cu($MeSCH_2CH_2SMe$)$_2$][$BF_4$]$_2$ (2.315—2.309 Å) [12] as well as the short copper–sulphur bond in bis[3,4-bis(2-

aminoethylthio)toluene]-μ-chloro-chlorodicopper(II) diperchlorate [2.445(8) Å].[10] Values in the five-coordinate square-pyramidal $[\mathrm{CuL}^4]^{2+}$ ion [6] are 2.38(1) for equatorial, 2.47(1) Å for axial although these bonds may be affected by steric constraints of the macrocyclic ligand as well as Jahn–Teller distortion. In contrast the nickel–sulphur distances [Ni–S(4) 2.393(6), Ni–S(7) 2.437(8) Å] are of similar length, that *trans* to Br(1) being the longer. These distances are equivalent to those seen in $[\mathrm{NiCl}\text{-}\mathrm{L}^2]^+$ [2.470(5) Å],[3] $[\mathrm{NiBrL}^3]^+$ [2.456(2) Å],[4] and $[\mathrm{NiCl}\text{-}\mathrm{L}^3]^+$ [2.472(5) Å] [5] where the nickel atoms, as stated earlier, are bonded to one sulphur atom of a disulphide group. Similar nickel–sulphur distances are seen in a whole range of compounds containing ligands based upon thiourea.[11]

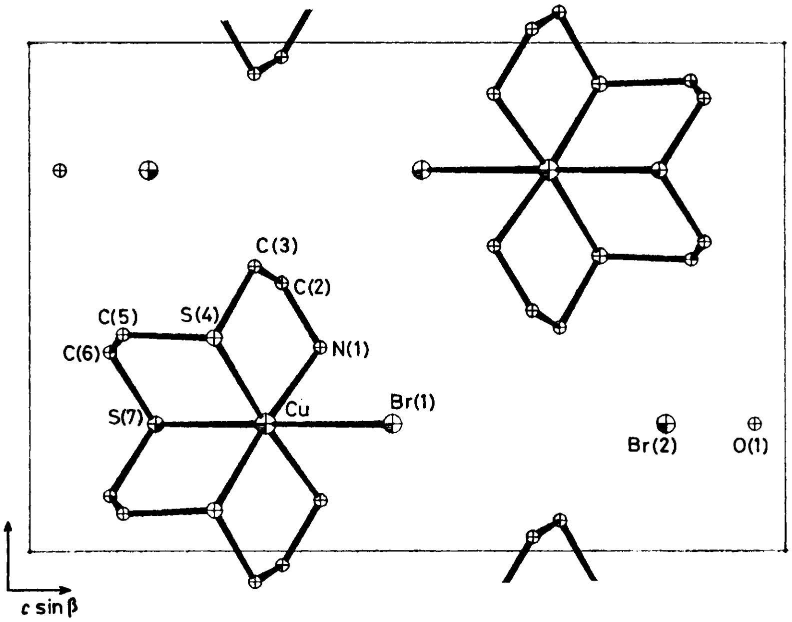

FIGURE 1 The unit cell of $[\mathrm{CuBrL}^1]\mathrm{Br{\cdot}H_2O}$ in the *a* projection

The metal–nitrogen distances in both structures are unremarkable being equivalent to those found in a vast number of species.[11]

The copper–bromine bond, that is one of the long axial bonds, is remarkably long [3.130(5) Å] especially for a terminal bond. Similar long bonds have been observed in[2-(aminomethyl)pyridine]dibromocopper(II) [3.260(6) Å] and dibromo(1,2-diamino-2-methylpropane)-copper(II) [3.109(2) Å] but in these latter structures each

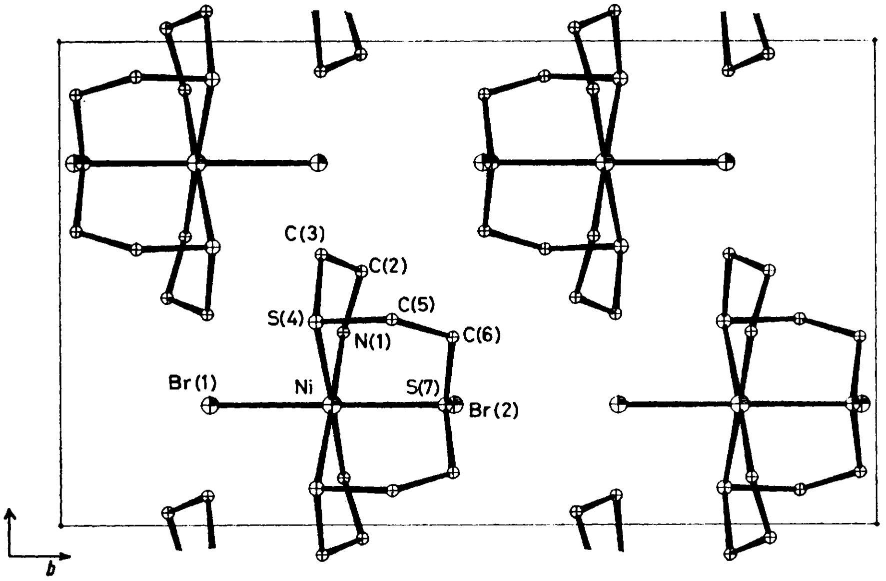

FIGURE 2 The unit cell of $[\mathrm{NiBrL}^1]\mathrm{Br}$ in the *c* projection

bromine atom forms one short and two long bonds to copper atoms.[13] The long Cu–Br(1) and Cu–S(7) distances in the present structure cannot be attributed to non-bonded interactions with hydrogen atoms as these would be the same in the nickel complex where no elongation is observed. The elongation in Cu–Br(1) is longer than that in the mutually *trans* Cu–S(7) (*ca.* 0.53 against 0.23 Å); possibly the position of S(7) is constrained by the rest of the atoms in the ligand.

TABLE 6

Least-squares planes. Distances (Å) of atoms from the various planes are quoted in square brackets. Atoms marked with an asterisk do not contribute to the plane

Plane 1: M, N(1), S(4)
[M = Cu: C(2)* 0.72, C(3)* 0.18; M = Ni: C(2)* 0.49, C(3)* −0.11]
Plane 2: M, S(4), S(7)
[M = Cu: C(5)* 0.35, C(6)* −0.19; M = Ni: C(5)* 0.31, C(6)* −0.20]
Plane 3: M(1), S(4), N($1^{I}$), S($4^{I}$)
[M = Cu: Cu* 0.18; M = Ni: Ni* 0.01]

The nickel–bromine distance [2.578(5) Å] is within the range of those reported in the literature and is similar to that in $[NiBrL^3]^+$[2.544(1) Å].[4] Least-squares planes (Table 6) show that the Ni atom is coplanar with the $N_2S_2$ plane. Not surprisingly this is not true for the Cu atom which is 0.18 Å above the equivalent plane being towards S(7).

TABLE 7

Ultraviolet–visible spectra, magnetic and conductivity data

| Compound | Band position [a] ($cm^{-1}$) |
|---|---|
| $[NiIL^1]I$ | 9 480, 10 255 $[^3T_{2g}(F)\leftarrow{}^3A_{2g}]$, 16 130 (sh) $(^1E_g\leftarrow{}^3A_{2g})$, 19 050, 20 000 $[^3T_{1g}(F)\leftarrow{}^3A_{2g}]$, 28 570 (sh) $[^3T_{1g}(P)\leftarrow{}^3A_{2g}]$, $\mu_B$ = 3.08 B.M., $Dq$ = 987 $cm^{-1}$, $B$ = 1 233 $cm^{-1}$ |
| $[NiBrL^1][ClO_4]$ | 9 710, 10 640 $[^3T_{2g}(F)\leftarrow{}^3A_{2g}]$, 16 930 (sh) $(^1E_g\leftarrow{}^3A_{2g})$, 18 690 $[^3T_{1g}(F)\leftarrow{}^3A_{2g}]$, $\mu_B$ = 3.03 B.M. |
| $[NiBrL^1]Br$ | 9 700, 10 650 $[^3T_{2g}(F)\leftarrow{}^3A_{2g}]$, 16 390 (sh) $(^1E_g\leftarrow{}^3A_{2g})$, 18 180(37) $[^3T_{1g}(F)\leftarrow{}^3A_{2g}]$, 28 490(31) $(^3T_{2g}\leftarrow{}^3A_{2g})$, $\mu_B$ = 3.00 B.M., $Dq$ = 1 017 $cm^{-1}$, $B$ = 1 076 $cm^{-1}$, $\Lambda$ = 78.1 S $cm^2$ $mol^{-1}$ [b] |
| $[Ni(NCS)L^1][NCS]$ | 10 415 (sh), 11 495 $[^3T_{2g}(F)\leftarrow{}^3A_{2g}]$, 16 500 (sh) (14) $(^1E_g\leftarrow{}^3A_{2g})$, 18 400 (35) $[^3T_{1g}(F)\leftarrow{}^3A_{2g}]$, 28 570 (sh) (85) $[^3T_{1g}(P)\leftarrow{}^3A_{2g}]$, $\mu_B$ = 3.10 B.M., $Dq$ = 1 095 $cm^{-1}$, $B$ = 944 $cm^{-1}$, $\Lambda$ = 60.7 S $cm^2$ $mol^{-1}$ [b] |
| $[NiBrL^1][PF_6]$ | 9 700, 10 610 $[^3T_{2g}(F)\leftarrow{}^3A_{2g}]$, 16 390 (sh) $(^1E_g\leftarrow{}^3A_{2g})$, 18 520 $[^3T_{1g}(F)\leftarrow{}^3A_{2g}]$, 27 400 $[^3T_{1g}(P)\leftarrow{}^3A_{2g}]$, $\mu_B$ = 3.06 B.M. |
| $[CuBrL^1]Br{\cdot}H_2O$ | 11 760 (sh) (46), 13 290br (83), 14 930 (sh) (80) $(^2T_{2g}\leftarrow{}^2E_g)$, $\mu_B$ = 1.54 B.M., $\Lambda$ = 70.0 S $cm^2$ $mol^{-1}$ [b] |
| $[Cu(NCS)L^1][NCS]$ | 11 110 (sh), 15 150 $(^2T_{2g}\leftarrow{}^2E_g)$, $\mu_B$ = 1.90 B.M. |
| $[CuBrL^1][ClO_4]$ | 11 170, 14 260 $(^2T_{2g}\leftarrow{}^2E_g)$, $\mu_B$ = 1.62 B.M. |
| $[CuIL^1]I$ | 14 285, 15 385 $(^2T_{2g}\leftarrow{}^2E_g)$, $\mu_B$ = 1.80 B.M. |
| $[CuBrL^1][PF_6]$ | 14 750br $(^2T_{2g}\leftarrow{}^2E_g)$, $\mu_B$ = 1.56 B.M. |

[a] Numbers in brackets are $\varepsilon_{max.}$ values (10 $m^2$ $mol^{-1}$) for those species with sufficient solubility in MeOH. Bands at higher energy were judged to be charge transfer in origin from $\varepsilon_{max.}$ values. [b] Conductivity measurements carried out in MeOH where $\Lambda$ (for KI) = 89 S $cm^2$ $mol^{-1}$.

The configuration of the five donor atoms in the quinquedentate ligand around the metal is αα (Figures 1 and 2) with $C_s$ symmetry. This αα configuration is also found in $[CoClL^5]^{2+}$ ($L^5$ = tetraethylenepentaamine) [14,15] where in addition to the αα form the αβ, ββ, and β *trans* forms are observed. These descriptions refer, of course, solely to the denticity of the ligand around the metal. The conformation of the ligand in the present structure is the same as that observed in the αα cobalt complex, as deduced from the signs and qualitative values of the torsion angles.* There are, not surprisingly, differences in the values of these angles for $L^1$ in $[CuBrL^1]^+$ and $L^5$ in $[CoClL^5]^{2+}$ but clearly the observed conformation must be remarkably stable as it is retained even when NH groups are substituted for S atoms.

In both structures the van der Waals distances between cations and anions are observed. In the copper compound the water molecule and the bromide ion are at short distances O(1) · · · Br(2) (3.24 Å), O(1) · · · Br($2^{II}$) (3.31 Å) with a Br · · · O · · · Br angle of 116.2° which implies strong hydrogen bonding. In addition the cations form chains [similar in type to those formed by Br(2) and O(1) see above] along *a* (= 5.56 Å) with N(1) · · · Br($1^{III}$) contacts of 3.47 Å and N(1)–H(1) · · · Br($1^{III}$) angles of 159.6° thus indicating some weak hydrogen-bond interaction.

There is no water molecule in the nickel compound so the anion Br(2) forms weak interactions with N(1) [Br($2^{II}$) · · · N(1) 3.45 Å; Br($2^{II}$) · · · H(1)–N(1) 165.4°].

All the nickel and copper compounds whose analytical data are given in Table 5 we believe to contain anions of the type $[MXL^1]^+$. Thus conductivity measurements on methanolic solutions of $[NiBrL^1]Br$ and $[Ni(NCS)L^1][NCS]$ gave $\Lambda$ values close to that of KI in methanol. The u.v.–visible spectra of $[NiBrL^1]X$, X = $ClO_4$, Br, or $PF_6$, were identical, as were their room-temperature magnetic moments (3.01 B.M.).† Infrared spectroscopic measurements on $[Ni(NCS)L^1][NCS]$ indicated the presence of both ionic and nitrogen co-ordinated thiocyanate and similarly the i.r. spectra of $[NiBrL^1]X$ (X = $PF_6$ or $ClO_4$) suggest $X^-$ is ionic.

The u.v.–visible spectra of the nickel compounds are recorded together with the band assignments in Table 7. The $^3T_{2g}\leftarrow{}^3A_{2g}$ bands shifts to higher energy on going along the series $[NiIL^1]^+$, $[NiBrL^1]^+$ reflecting the positions of the anions in the spectrochemical series. All the bands are split resulting from the lifting of the degeneracy of the $^3T_{2g}$ level in the low-symmetry co-

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* Signs for the angles are incorrectly given in ref. 15.

† Throughout this paper: 1 B.M. = 9.274 × $10^{-24}$ A $m^2$.

ordination sphere of the nickel ion. The position of the third spin-allowed band was determined by measurements of $\varepsilon_{max.}$ values for $[NiXL^1]^+$ (X = Br or NCS) and the assignment confirmed by the calculation of the Racah parameter $B$ and $10Dq$ (see Table 7).[16]

As with the related nickel compounds the series $[CuBrL^1]X$ (X = Br, $ClO_4$, or $PF_6$) have identical u.v.-visible spectra and their i.r. spectra indicate the presence of unco-ordinated ions (X = $ClO_4$ or $PF_6$). The reaction involving exchange of $I^-$ for $Br^-$ gave $[CuIL^1]I$ a copper(II) compound (magnetic moment 1.58 B.M.) with no evidence for reduction to copper(I). In contrast exchange reactions with $NCS^-$ leading to the isolation of $[Cu(NCS)L^1][NCS]$ had to be restricted to gently heating a methanolic solution of $[CuBrL^2]Br$ and Li[NCS] for 5 min for if heating was extended to 10 min partially reduced species were obtained. The u.v.-visible spectra of $[CuXL^1]^+$ (X = Br, I, or NCS) show as expected from the structural studies more than one band assignable to *d–d* transitions. Curiously the first band in $[CuIL^2]^+$ is at higher energy than those in $[CuBrL^2]^+$ and $[Cu(NCS)L^2]^+$.

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