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# Synthesis and Characterization of Complexes of Aluminum Halide with 2,2′-Bipyridine, 1,10-Phenanthroline, and 2,2′,2″-Terpyridine in Acetonitrile

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*Received August 17, 1976* AIC60595G

The reactions of aluminum halides with 2,2′-bipyridine (bpy, BB), 1,10-phenanthroline (phen, BB), and 2,2′,2″-terpyridine (terpy, BBB) in acetonitrile have been studied. Adducts of general formulas $AlX_3 \cdot 2BB$ (X = Cl, Br) and $AlI_3 \cdot 3BB$ were formed with bpy and phen and those of formula $AlX_3 \cdot 2BBB$ (X = Br, I) with terpy. In the presence of a large excess of phen, $AlBr_3 \cdot 3phen$ was obtained. Spectroscopic and conductance measurements suggest the formulations $[AlX_2(BB)_2]X$ and $[Al(BB)_3]X_3$ for the bpy and phen adducts and $[Al(BBB)_3]X_3$ for the terpy adducts. The solid-state structure of $AlCl_3 \cdot 2bpy \cdot CH_3CN$ has confirmed the formulation $[AlCl_2(bpy)_2]Cl \cdot CH_3CN$; the octahedral cation is the cis isomer with approximate $C_2$ symmetry. The Cl–Al–Cl angle is 96.35 (6)° and the mean Al–Cl bond distance is 2.255 (2) Å. Both 2,2′-bipyridine ligands are bidentate with a mean N–Al–N angle of 79.5 (1)°; Al–N bond distances cis to Cl are 2.025 (3) Å and Al–N bond distances trans to Cl are 2.040 (3) Å.

## Introduction

Adducts of the heavier group 3 halides with polydentate nitrogen bases are well-known.[1] Complexes with four different stoichiometries have been reported from reactions of $MX_3$ (M = Ga, In, Tl) with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2′,2″-terpyridine (terpy) in a variety of solvents. The adducts that have been reported include $MX_3 \cdot BB$, $MX_3 \cdot 1.5BB$, $MX_3 \cdot 2BB$, $MX_3 \cdot 3BB$ (BB = bpy or phen), and $MX_3 \cdot BBB$ (BBB = terpy). In general these adducts have been formulated as the ionic species $[MX_2(BB)_2]MX_4$ for the 1:1 adducts, $[MX_2(BB)_2][MX_4(BB)]$ for the 1:1.5 adducts, $[MX_2(BB)_2]X$ for the 1:2 adducts and $[M(BB)_3]X_3$ for the 1:3 adduct on the basis of conductometric and spectroscopic studies.

Until our recent preliminary study no reactions of bpy with aluminum halides had been reported.[2] The complexes obtained from these reactions as well as with terpy and phen are described and conductivity and spectral measurements are reported in this study. A solid-state x-ray structural study of $[AlCl_2(bpy)_2]Cl \cdot CH_3CN$ has been completed.

## Experimental Section

**General Data.** Commercial $AlCl_3$ was sublimed twice under vacuum and stored in sealed ampules. Commercial $AlBr_3$ was distilled from aluminum foil and stored in sealed ampules. $AlBr_3$ samples that developed a brown color were repurified. $AlI_3$ was prepared by an established procedure[3] and sublimed over aluminum at 600 °C until a white product was obtained. Commercial 2,2′-bipyridine and 2,2′,2″-terpyridine were used as supplied. 1,10-Phenanthroline was dried by dissolving samples in benzene and removing the benzene–water azeotrope followed by recrystallization from benzene. Acetonitrile was heated at reflux over phosphorus pentoxide for 48 h followed by distillation.

Carbon analyses were obtained on a total organic carbon analyzer, the percent aluminum was determined by atomic absorption, and the halogen content was determined by the Volhard method. Analytical data for the isolated adducts are given in Table I. The infrared spectra were obtained as KBr disks and Nujol mulls on a Perkin-Elmer Model 337 spectrophotometer and are given in Table II. Ultraviolet spectra were obtained on a Perkin-Elmer Model 201 spectrophotometer and conductivity measurements were carried out in a 10-ml conductivity cell (cell constant 0.145) using a Yellow Springs Instrument Model 31 conductivity bridge. Freshly prepared solutions of base and aluminum halide in acetonitrile were mixed at various acid:base ratios and the volume was adjusted to 10 ml. The acid concentration was constant at $10^{-3}$ M. All measurements were made in a nitrogen-filled drybox. Ultraviolet spectral data and conductivity data are given in Table III.

**Adduct Formation.** Adducts were obtained from reactions with acid:base mole ratios of 1:2, 1:3, and 1:10 in a nitrogen-filled inert-atmosphere chamber. One gram or less of aluminum halide and a corresponding molar excess of base were dissolved in approximately 25 ml of acetonitrile. The aluminum halide solution was added dropwise to the stirred base solution. Precipitation of the adducts usually occurred a few minutes after the aluminum halide solution was added. The product was filtered and washed with acetonitrile. Adducts were allowed to dry in a nitrogen atmosphere. Attempts to recrystallize the adducts from a variety of nonprotonic solvents failed. The adducts were insoluble in acetonitrile and other nonprotonic solvents such as benzene, nitrobenzene, and hexane but were soluble in anhydrous ethanol and methanol and recoverable from the latter solvent.

**Structure Determination of $[Al(C_{10}H_8N_2)_2Cl_2]Cl \cdot CH_3CN$.** A single crystal in the form of a rectangular parallelepiped with dimensions of 0.22 × 0.24 × 0.48 mm was mounted in a glass capillary and held on the wall with a small amount of silicone grease. Rotation photographs and systematic absences for $h0l$, $l$ odd, and $0k0$, $k$ odd, uniquely determined the space group $P2_1/c$. Lattice constants were obtained from least-squares refinement of 15 reflections with $2\theta$ between 20 and 43° centered on a Syntex $P2_1$ diffractometer with Mo K$\alpha$ radiation ($\lambda$ 0.71069 Å) which had been diffracted from a highly oriented graphite crystal whose diffraction vector was parallel to that of the crystal. The unit cell parameters are $a = 6.946$ (2) Å, $b = 11.012$ (2) Å, $c = 29.712$ (7) Å, $\beta = 99.14$ (2)°, $\rho$(calcd) = 1.44 g/cm$^3$, $\rho$(flotation) = 1.43 g/cm$^3$, $Z = 4$ formula units, and $\mu = 4.69$ cm$^{-1}$.

Intensity data to $(\sin\theta)/\lambda < 0.595$ were collected by the $\theta$–$2\theta$ technique with a scan rate of 2° min$^{-1}$. Backgrounds were measured at each end of the scan ($2\theta$ scan range: $2\theta(\text{MoK}\alpha_1) - 1.0$ to $2\theta(\text{MoK}\alpha_2) + 1.0°$) for a total time equal to half the scan time. During data collection, the intensities of three standard reflections were measured every 97 reflections with no significant variation in intensity observed. Standard deviations[6] were assigned to the intensities according to the formula $\sigma(I) = [\sigma_{\text{counter}}I^2 + (0.03I)^2]^{1/2}$, where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, $I$ is the net intensity, $K$ is the ratio of scan time to background time, and $B$ is the total background counts. No corrections for absorption were made. Of the 4319 independent data examined, 2487 had $I > 3\sigma(I)$ and were used in the solution and refinement process.

The structure was solved by an iterative application of the Sigma-2 relationship using 233 normalized structure factors of magnitude 1.5 or greater. An $E$ map based on the set of phases for the solution with the largest consistency index (0.87) revealed the locations of the majority of atoms in the structure. Successive Fourier syntheses yielded the positions of all 31 nonhydrogen atoms including an acetonitrile molecule of crystallization. The hydrogen atoms on the bipyridine ligands were included in the calculations at ideal locations with fixed distances of 1.0 Å and isotropic thermal parameters 10% larger than the equivalent isotropic $B$ of the carbon atom to which they are bonded (range 3.2–4.4 Å$^2$). A difference Fourier synthesis provided the positions of the three hydrogen atoms on the acetonitrile molecule. Full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for the three acetonitrile hydrogen atoms (bipyridine hydrogen atoms with fixed locations and thermal parameters) yielded $R = \sum\|F_o| - |F_c\|/\sum|F_o| = 0.039$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.044$. The error of fit was 1.64 and the maximum residual electron density was 0.31 e/Å$^3$. Atomic scattering factors and real and imaginary

Table I. Adducts Formed from the Reaction of $AlX_3$ with 1,10-Phenanthroline and 2,2′,2″-Terpyridine in Acetonitrile[a]

| | | % calcd[b] | | | % found | | |
|---|---|---|---|---|---|---|---|
| Compd | Mp, °C | C | X | Al | C | X | Al |
| $AlCl_3$·2phen[c] | 235 | 58.2 (58.4) | 21.5 (19.9) | 5.4 (5.0) | 55.5 | 22.1 | 4.1 |
| $AlBr_3$·2phen[c] | >300 | 45.9 (46.7) | 38.2 (35.9) | 4.3 (4.0) | 45.4 | 36.0 | 3.9 |
| $AlBr_3$·3phen[d] | >300 | 53.4 (53.6) | 29.7 (28.2) | 3.3 (3.2) | 50.0 | 30.6 | 3.8 |
| $AlI_3$·3phen[c] | 210 | 45.5 (46.0) | 40.1 (38.4) | 2.8 (2.7) | 43.5 | 40.4 | |
| $AlBr_3$·3bpy[d] | >300 | 49.0 (49.4) | 32.6 (30.9) | 3.7 (3.5) | 45.9 | 32.8 | 4.0 |
| $AlCl_3$·terpy[c] | | 49.2 (50.0) | 29.1 (26.1) | 7.4 (6.6) | 50.2 | 27.9 | |
| $AlBr_3$·2terpy[c,e] | | 49.1 (49.6) | 32.7 (31.0) | 3.7 (3.5) | 48.0 | 30.7 | 4.0 |
| $AlI_3$·2terpy[c,f] | >300 | 41.2 (42.0) | 43.6 (41.6) | 3.1 (3.0) | 43.0 | 37.6 | 3.5 |

[a] Data for 1:2 adducts with bipyridine were reported previously.[2] [b] Values in parentheses are for adducts containing 1 mol of acetonitrile. [c] Adducts from 1:2 acid:base ratio. [d] Adducts from 1:10 acid:base ratio. [e] $\% N_{calcd} = 11.5$; $\% N_{exptl} = 9.54$. [f] $\% N_{calcd} = 9.6$; $\% N_{exptl} = 9.3$.

Table II. Infrared Absorption Frequencies ($cm^{-1}$) for the Adducts of $AlX_3$ with 2,2′-Bipyridine, 1,10-Phenanthroline, and 2,2′,2″-Terpyridine[a]

| Compd | C=C, C=N[b] | C–H | |
|---|---|---|---|
| 2,2′-Bipyridine | 1560, 1415 | 760 | 430 |
| $AlCl_3$·2bpy | 1575, 1450 | 780 | 420 |
| $AlBr_3$·2bpy | 1565, 1445 | 773 | 450 |
| $AlI_3$·3bpy | 1565, 1445 | 775 | 445 |
| 1,10-Phenanthroline | 1590, 1500, 1493 | 850, 725 | 415 |
| $AlCl_3$·2phen | 1590, 1525, 1440 | 850, 725 | 460 |
| $AlBr_3$·2phen | 1595, 1530, 1435 | 855, 727 | 450 |
| $AlBr_3$·3phen | 1595, 1540, 1435 | 855, 725 | 466 |
| $AlI_3$·3phen | 1600, 1535, 1440 | 855, 725 | 467 |
| 2,2′,2″-Terpyridine | 1570, 1550, 1440, 1410 | 765 | |
| $AlCl_3$·terpy | 1580, 1550, 1455, 1430 | 775 | 441 |
| $AlBr_3$·2terpy | 1610, 1570, 1480, 1455 | 774 | 444 |
| $AlI_3$·2terpy | 1594, 1564, 1470, 1444 | 768 | 444 |

[a] KBr disk. See ref 4. [b] A discussion of this region of the spectrum is given in ref 5.

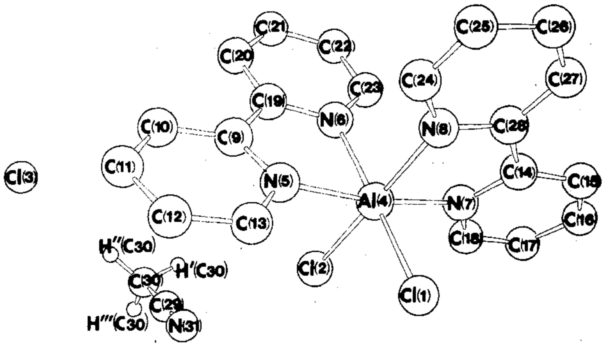

Figure 1. Structure of $[AlCl_2(bpy)_2]Cl·CH_3CN$. The atom numbering scheme used in the tables is defined.

anomalous dispersion corrections for Cl and Al were taken from ref 7. Atomic parameters for the nonhydrogen atoms are given in Table IV.

## Description of the Structure

The structure of $AlCl_3·2bpy$ consists of distorted octahedral *cis*-dichlorobis(bipyridine)aluminum cations with approximate $C_2$ symmetry, chloride anions, and a free acetonitrile solvate molecule. A drawing of the structure is given in Figure 1 with the numbering scheme that has been used. Figure 2 is a stereoscopic drawing of the asymmetric part of the structure.

Table III. Ultraviolet Absorption Maxima and Molar Conductance Values of Solutions of $AlX_3$ Containing 2,2′-Bipyridine, 1,10-Phenanthroline, and 2,2′,2″-Terpyridine[a]

| Acid | Base | $\lambda_{max}$, nm | $\Lambda_M$, $\Omega^{-1}$ $cm^2$ $mol^{-1}$ |
|---|---|---|---|
| $AlCl_3$ | | | 65[b] |
| $AlBr_3$ | | | 56[b] |
| $AlI_3$ | | | 276[b] |
| | bpy | 237, 280 | |
| $AlCl_3$ | 2bpy | 243, 303 | 86 |
| $AlBr_3$ | 2bpy | 240, 309 | 146 |
| $AlI_3$ | 3bpy | *c* | 304 |
| | phen | 230, 263 | |
| $AlCl_3$ | 2phen | 229, 274 | 99 |
| $AlBr_3$ | 2phen | 228, 272 | 160 |
| $AlI_3$ | 3phen | *c* | 268[d] |
| | terpy | 235, 278 | |
| $AlCl_3$ | terpy | 214, 237, 282, 325 | 65 |
| $AlBr_3$ | 2terpy | 217, 238, 290, 327 | 174[e] |
| $AlI_3$ | 2terpy | 215, 247, 290, 329 | 304[f] |

[a] Solutions were prepared by mixing 1-ml quantities of freshly prepared $10^{-2}$ M $AlX_3$ solutions with the appropriate molar amount of base and diluting to 10 ml. UV measurements were made by dilution of the solutions prepared for conductivity measurements to $10^{-4}$ or $10^{-5}$ M. Conductance of $CH_3CN$ used for measurements was 7 $\mu\Omega^{-1}$ for $AlCl_3$ and $AlI_3$ and 15 $\mu\Omega^{-1}$ for $AlBr_3$. [b] $10^{-3}$ M $AlX_3$. [c] Bipyridine absorption obscured by intense bands at 240 nm attributed to free $I^-$. [d] Solution became cloudy during measurement. [e] Value at 1:1 mole ratio was 131. [f] Value at 1:1 mole ratio was 283.

Interatomic bond lengths and angles are presented in Table V. The mean Al–Cl bond length is 2.255 (2) Å. For the Al–N bonds trans to the chlorine atoms, the mean bond length is 2.040 (3) Å which is slightly longer than the mean value 2.025 (3) Å for Al–N bonds cis to the chlorine atoms.

Within the bipyridine ligands the mean C–N distance is 1.353 (4) Å [range 1.346–1.359 Å]; the mean C–C distance in the rings is 1.381 (5) Å [range 1.368–1.393 Å]; the mean C–C bond length joining the pyridine rings is 1.483 (5) Å. The twist angles about the C–C bonds in the two bipyridine ligands

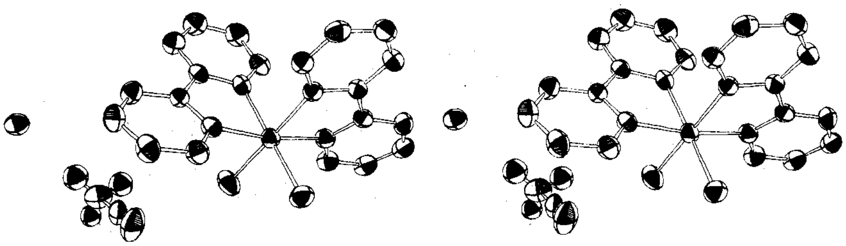

Figure 2. Stereoscopic view of the $[AlCl_2(bpy)_2]Cl·CH_3CN$ structure. All atoms included in the refinement have been drawn with 50% probability ellipsoids.

**Table IV.** Positional and Thermal Parameters[a] ($\times 10^4$) for Nonhydrogen Atoms[b]

| Atom | *x* | *y* | *z* | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cl(1) | 806 (1) | 4569 (1) | 771.6 (4) | 186 (2) | 64 (1) | 14.7 (2) | 12 (1) | 5.8 (5) | 3.6 (3) |
| Cl(2) | 971 (1) | 5712 (1) | 1826.1 (4) | 215 (3) | 105 (1) | 13.9 (2) | 34 (1) | 26 (1) | 14.3 (4) |
| Cl(3) | 5948 (2) | 5560 (1) | 4199.7 (4) | 238 (3) | 80 (1) | 13.8 (2) | −18 (1) | 7 (1) | −5.1 (3) |
| Al(4) | 2607 (2) | 5914 (1) | 1232.8 (4) | 143 (2) | 53 (1) | 8.8 (1) | 7 (1) | 6.2 (5) | 4.1 (3) |
| N(5) | 4581 (4) | 4675 (2) | 1527 (1) | 160 (7) | 44 (3) | 8.2 (4) | 2 (3) | 8 (1) | 0 (1) |
| N(6) | 4537 (4) | 7015 (3) | 1632 (1) | 168 (8) | 48 (3) | 7.8 (4) | 10 (4) | 10 (1) | 2 (1) |
| N(7) | 1002 (4) | 7322 (2) | 943 (1) | 152 (7) | 51 (3) | 9.6 (4) | 2 (4) | 7 (1) | 1 (1) |
| N(8) | 4075 (4) | 6299 (2) | 708 (1) | 139 (7) | 48 (3) | 8.2 (4) | −4 (4) | 4 (1) | 0 (1) |
| C(9) | 5858 (5) | 5092 (3) | 1884 (1) | 136 (8) | 57 (3) | 7 (1) | −1 (4) | 7 (2) | 2 (1) |
| C(10) | 7049 (5) | 4317 (3) | 2175 (1) | 158 (9) | 72 (4) | 10 (1) | 17 (5) | 4 (2) | 3 (1) |
| C(11) | 6942 (6) | 3083 (4) | 2091 (1) | 216 (11) | 71 (4) | 12 (1) | 28 (5) | 2 (2) | 6 (1) |
| C(12) | 5688 (6) | 2653 (3) | 1719 (1) | 239 (11) | 54 (4) | 14 (1) | 33 (5) | 9 (2) | 4 (1) |
| C(13) | 4506 (5) | 3463 (3) | 1443 (1) | 194 (10) | 53 (4) | 11 (1) | 4 (5) | 6 (2) | 1 (1) |
| C(14) | 1384 (5) | 7654 (3) | 527 (1) | 166 (9) | 41 (3) | 10 (1) | −15 (4) | 2 (2) | 2 (1) |
| C(15) | 160 (6) | 8429 (3) | 247 (1) | 201 (10) | 61 (4) | 11 (1) | 6 (5) | −2 (2) | 7 (1) |
| C(16) | −1455 (6) | 8910 (3) | 400 (2) | 186 (10) | 50 (4) | 15 (1) | −1 (5) | −7 (2) | 5 (1) |
| C(17) | −1799 (5) | 8627 (3) | 833 (2) | 154 (9) | 50 (3) | 15 (1) | 15 (5) | −1 (2) | −2 (1) |
| C(18) | −555 (5) | 7820 (3) | 1091 (1) | 171 (10) | 68 (4) | 11 (1) | 6 (5) | 8 (2) | −1 (1) |
| C(19) | 5870 (5) | 6431 (3) | 1940 (1) | 150 (9) | 53 (3) | 8 (1) | 1 (4) | 10 (2) | 0 (1) |
| C(20) | 7153 (6) | 7041 (3) | 2263 (1) | 207 (11) | 65 (4) | 11 (1) | −3 (5) | 4 (2) | −3 (1) |
| C(21) | 7099 (6) | 8301 (4) | 2272 (1) | 246 (12) | 79 (4) | 11 (1) | −22 (6) | 6 (2) | −6 (1) |
| C(22) | 5769 (6) | 8897 (3) | 1955 (1) | 282 (12) | 50 (4) | 13 (1) | −13 (5) | 11 (2) | −3 (1) |
| C(23) | 4516 (6) | 8241 (3) | 1642 (1) | 225 (11) | 53 (4) | 10 (1) | 0 (5) | 11 (2) | 3 (1) |
| C(24) | 5748 (5) | 5797 (3) | 624 (1) | 160 (9) | 58 (3) | 8.9 (5) | −1 (5) | 5 (2) | 0 (1) |
| C(25) | 6556 (5) | 6048 (3) | 240 (1) | 160 (9) | 75 (4) | 10 (1) | −20 (5) | 7 (2) | −6 (1) |
| C(26) | 5631 (6) | 6900 (3) | −67 (1) | 203 (10) | 74 (4) | 8 (1) | −31 (5) | 10 (2) | 0 (1) |
| C(27) | 3950 (6) | 7439 (3) | 17 (1) | 202 (10) | 68 (4) | 9 (1) | −10 (5) | 7 (2) | 5 (1) |
| C(28) | 3188 (5) | 7122 (3) | 403 (1) | 158 (9) | 54 (3) | 7.7 (5) | −13 (4) | 3 (2) | 2 (1) |
| C(29) | 108 (7) | 5944 (4) | 3454 (2) | 260 (12) | 92 (5) | 11 (1) | 23 (6) | −5 (2) | 6 (2) |
| C(30) | 541 (10) | 6625 (6) | 3871 (2) | 299 (17) | 103 (6) | 18 (1) | −10 (8) | 15 (3) | −11 (2) |
| N(31) | −162 (7) | 5399 (4) | 3134 (2) | 470 (16) | 161 (6) | 14 (1) | 23 (8) | −20 (3) | −4 (2) |

[a] In the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Standard deviations from the full variance–covariance matrix are given in parentheses for the least significant digit(s).

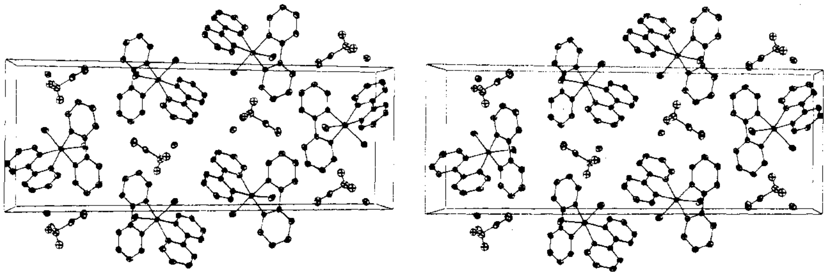

**Figure 3.** Packing diagram of the structure viewed down the *a* axis.

are 5.15 and 7.07°. The bipyridine ligand atoms, N(5) and N(6), are 2.02 and 0.20 Å, respectively, below the $AlCl_2$ plane; N(7) and N(8) are 2.01 and 0.16 Å above the $AlCl_2$ plane. The packing of cations, anions, and solvent molecules is shown in the stereoscopic view of the unit cell contents in Figure 3. The shortest nonbonded interaction involving atoms whose positional parameters were refined is 2.84 (6) Å between Cl(1) and H′(C30) related by the transformation $-x, -{}^1/_2 + y, {}^1/_2 - z$; the shortest packing distance between nonhydrogen atoms is 3.40 (1) Å between C(10) and N(31) related by $x + 1, y, z$.

A comparison of bond distances and angles about the metal atom in group 3 halide complexes is given in Table VI. A recent report[11] of the solid-state structure of $AlCl_3{\cdot}2CH_3CN$ has shown that the adduct is $[AlCl(CH_3CN)_5][AlCl_4]_2{\cdot}CH_3CN$. The Al–Cl bond distance in the $[AlCl(CH_3CN)_5]^{2+}$ cation is 2.197 (5) Å, significantly shorter than the Al–Cl distance in $[AlCl_2(bpy)_2]^+$.

## Discussion and Results

The reactions of group 3 halides with bidentate and tridentate nitrogen bases have been studied in a variety of solvents including acetonitrile, ethanol, methylene chloride, acetone, and ether. The adducts formed from the heavier group 3 halides are shown in Table VII, and those adducts which were formed in acetonitrile are so indicated. Although the stoichiometry of the reactions was not always specified, most were run at a 1:1 mole ratio of acid:base with the exception of a study of $GaX_3$ with 2,2′-bipyridine and 1,10-phenanthroline in $CH_3CN$[12] and of $InX_3$ with excess phen in $CH_3CN$.[25] When $GaX_3$ was reacted with a 3 molar excess of base in $CH_3CN$, the products obtained were "$Ga_3Cl_6(bpy)_4$", $GaBr_3(bpy)_2{\cdot}MeCN$, and $GaI_3{\cdot}bpy$ (obtained only after repeated recrystallization). Repeated recrystallization of the chloride adduct from a 1:1 mixture of acetone–acetonitrile gave $GaCl_3{\cdot}bpy$. The reaction of $InCl_3$ with excess phen in acetonitrile gave $InCl_3{\cdot}(phen)_{1.5}{\cdot}CH_3CN$.

The reaction of aluminum halides with 2,2′-bipyridine and 1,10-phenanthroline in acetonitrile at a 1:2 mole ratio produced the adducts $[AlX_2(BB)_2]X$ (X = Cl, Br) and $[Al(BB)_3]X_3$ (X = I) where BB = 2,2′-bipyridine and 1,10-phenanthroline.[2] No new adducts were obtained when the mole ratio was increased to 1:3 or decreased to 1:1. The reactions with excess base (1:10 mole ratio) produced $[AlCl_2(BB)_2]Cl$ and the new adduct $[Al(BB)_3]Br_3$. The aluminum chloride adducts are white, $AlBr_3{\cdot}3bpy$ is cream colored, and $AlBr_3{\cdot}3phen$ is yellow. The molecular adduct $AlCl_3{\cdot}terpy$ and the ionic complexes $[Al(terpy)_2]X_3$ (X = Br, I) were isolated from the reaction

**Table V.** Bond Lengths (Å) and Angles (deg)

Bond Lengths

| | | | |
|---|---|---|---|
| Cl(1)–Al(4) | 2.256 (2) | C(14)–C(15) | 1.384 (5) |
| Cl(2)–Al(4) | 2.255 (2) | C(14)–C(28) | 1.482 (5) |
| Al(4)–N(5) | 2.030 (3) | C(15)–C(16) | 1.381 (5) |
| Al(4)–N(6) | 2.042 (3) | C(16)–C(17) | 1.378 (6) |
| Al(4)–N(7) | 2.020 (3) | C(17)–C(18) | 1.384 (5) |
| Al(4)–N(8) | 2.038 (3) | C(19)–C(20) | 1.376 (5) |
| N(5)–C(9) | 1.352 (4) | C(20)–C(21) | 1.388 (5) |
| N(5)–C(13) | 1.357 (4) | C(21)–C(22) | 1.377 (5) |
| N(6)–C(19) | 1.356 (4) | C(22)–C(23) | 1.374 (5) |
| N(6)–C(23) | 1.351 (4) | C(24)–C(25) | 1.377 (5) |
| N(7)–C(14) | 1.357 (4) | C(25)–C(26) | 1.393 (5) |
| N(7)–C(18) | 1.347 (4) | C(26)–C(27) | 1.368 (5) |
| N(8)–C(24) | 1.346 (4) | C(27)–C(28) | 1.381 (5) |
| N(8)–C(28) | 1.359 (4) | C(29)–C(30) | 1.439 (7) |
| C(9)–C(10) | 1.390 (5) | C(29)–N(31) | 1.116 (5) |
| C(9)–C(19) | 1.483 (5) | C(30)–H′(C30) | 1.00 (5) |
| C(10)–C(11) | 1.381 (5) | C(30)–H″(C30) | 1.05 (5) |
| C(11)–C(12) | 1.378 (5) | C(30)–H‴(C30) | 0.84 (5) |
| C(12)–C(13) | 1.389 (5) | | |

Bond Angles

| | | | |
|---|---|---|---|
| Cl(1)–Al(4)–Cl(2) | 96.4 (1) | C(10)–C(11)–C(12) | 119.5 (4) |
| Cl(1)–Al(4)–N(5) | 95.3 (1) | C(11)–C(12)–C(13) | 119.5 (4) |
| Cl(1)–Al(4)–N(6) | 172.8 (1) | N(5)–C(13)–C(12) | 121.4 (4) |
| Cl(1)–Al(4)–N(7) | 91.7 (1) | N(7)–C(14)–C(15) | 121.5 (3) |
| Cl(1)–Al(4)–N(8) | 88.2 (1) | N(7)–C(14)–C(28) | 114.6 (3) |
| Cl(2)–Al(4)–N(5) | 89.3 (1) | C(15)–C(14)–C(28) | 123.9 (3) |
| Cl(2)–Al(4)–N(6) | 88.3 (1) | C(14)–C(15)–C(16) | 119.5 (4) |
| Cl(2)–Al(4)–N(7) | 95.5 (1) | C(15)–C(16)–C(17) | 119.3 (4) |
| Cl(2)–Al(4)–N(8) | 173.6 (1) | C(16)–C(17)–C(18) | 118.5 (4) |
| N(5)–Al(4)–N(6) | 79.2 (1) | N(7)–C(18)–C(17) | 122.9 (4) |
| N(5)–Al(4)–N(7) | 171.0 (1) | N(6)–C(19)–C(9) | 113.9 (3) |
| N(5)–Al(4)–N(8) | 94.8 (1) | N(6)–C(19)–C(20) | 122.4 (3) |
| N(6)–Al(4)–N(7) | 93.3 (1) | C(9)–C(19)–C(20) | 123.7 (3) |
| N(6)–Al(4)–N(8) | 87.6 (1) | C(19)–C(20)–C(21) | 119.0 (4) |
| N(7)–Al(4)–N(8) | 79.9 (1) | C(20)–C(21)–C(22) | 118.7 (4) |
| Al(4)–N(5)–C(9) | 115.1 (2) | C(21)–C(22)–C(23) | 119.8 (4) |
| Al(4)–N(5)–C(13) | 125.3 (3) | N(6)–C(23)–C(22) | 122.2 (4) |
| C(9)–N(5)–C(19) | 118.7 (3) | N(8)–C(24)–C(25) | 123.2 (3) |
| Al(4)–N(6)–C(19) | 115.2 (2) | C(24)–C(25)–C(26) | 118.3 (3) |
| Al(4)–N(6)–C(23) | 126.7 (3) | C(25)–C(26)–C(27) | 119.3 (3) |
| C(19)–N(6)–C(23) | 117.9 (3) | C(26)–C(27)–C(28) | 119.6 (3) |
| Al(4)–N(7)–C(14) | 114.9 (2) | N(8)–C(28)–C(14) | 114.2 (3) |
| Al(4)–N(7)–C(18) | 126.3 (3) | N(8)–C(28)–C(27) | 122.0 (3) |
| C(14)–N(7)–C(18) | 118.1 (3) | C(14)–C(28)–C(27) | 123.8 (3) |
| Al(4)–N(8)–C(24) | 127.4 (2) | C(30)–C(29)–N(31) | 177.5 (7) |
| Al(4)–N(8)–C(28) | 114.9 (2) | C(29)–C(30)–H′(C30) | 103 (3) |
| C(24)–N(8)–C(28) | 117.6 (3) | C(29)–C(30)–H″(C30) | 106 (3) |
| N(5)–C(9)–C(10) | 122.1 (3) | C(29)–C(30)–H‴(C30) | 106 (4) |
| N(5)–C(9)–C(19) | 114.6 (3) | H′(C30)–C(30)–H″(C30) | 116 (4) |
| C(10)–C(9)–C(19) | 123.3 (3) | H′(C30)–C(30)–H‴(C30) | 108 (5) |
| C(9)–C(10)–C(11) | 118.9 (4) | H″(C30)–C(30)–H‴(C30) | 116 (5) |

**Table VI.** Comparison of Bond Distances and Angles about the Metal Atom in Group 3 Halide Complexes of 2,2′-Bipyridine and 1,10-Phenanthroline

| | $[AlCl_2(bpy)_2]Cl$ | $[GaCl_2(bpy)_2][GaCl_4]$[8] | $[InCl_2(bpy)(acac)]$[9] | $[TlCl_3(phen)]_2$[10] |
|---|---|---|---|---|
| M–Cl, Å | $2.255^a$ | $2.265^b$ | $2.418^a$ | $2.450^{a,c}$ |
| M–N,$^d$ Å | $2.025^a$ | 2.095 | $2.299^e$ | $2.364^{a,f}$ |
| M–N,$^g$ Å | $2.040^a$ | 2.111 | $2.276^h$ | |
| Cl–M–Cl, deg | 96.4 | 97.3 | 96.8 | $104.6^c$ |
| Cl–M–N,$^i$ deg | $91.4^a$ | $92.6^a$ | $93.6^a$ | $94.8^{a,c}$ |
| Cl–M–N,$^j$ deg | $173.2^a$ | 169.9 | $165.1^k$ | $150.2^{c,k}$ |
| N–M–N, deg | $79.5^{a,l}$ | $77.2^l$ | 71.7 | 71.5 |

[a] Mean value. [b] Cation distance. [c] Terminal Cl atoms only. [d] N atom(s) cis to both Cl atoms. [e] In–O distance for O atom cis to both Cl atoms is 2.124 Å. [f] Each N atom is trans to one Cl atom and cis to three Cl atoms. [g] N atom(s) cis to one Cl atom and trans to one Cl atom. [h] In–O distance for O atom cis to one Cl atom and trans to one Cl atoms is 2.164 Å. [i] N atom(s) cis to Cl atoms. [j] N atom(s) trans to Cl atoms. [k] Calculated from published atomic coordinates. [l] N atoms in the same bidentate.

**Table VII.** Adducts Formed between Gallium, Indium, and Thallium Halides and 2,2′-Bipyridine, 1,10-Phenanthroline, and 2,2′,2″-Terpyridine

| Adduct | Base | Acid |
|---|---|---|
| $MX_3 \cdot BB$ | bpy | $GaX_3$ (X = Cl, I),$^{a,12}$ $TlX_3$ (X = Cl, Br, I)$^{a,13,14}$ |
| | phen | $GaX_3$ (X = Cl, Br, I),$^{15}$ $TlX_3$ (X = Cl, Br, I)$^{a,13,14,16}$ |
| $MX_3 \cdot 1.5BB$ | bpy | $InX_3$ (X = Cl, Br, I)$^{a,17,18}$ |
| | phen | $InCl_3$,$^{a,18}$ $TlBr_3$$^{a,19}$ |
| $MX_3 \cdot 2BB$ | bpy | $GaBr_3$$^{12}$ |
| | phen | $GaX_3$ (X = Cl, Br),$^{20}$ $InX_3$ (X = Cl, Br, I),$^{b,21}$ $TlI_3$$^{a,14}$ |
| $MX_3 \cdot 3BB$ | bpy | $InX_3$ (X = Cl, Br, I)$^{21}$ |
| | phen | $GaX_3$ (X = Cl, Br, I),$^{20,22}$ $InX_3$ (X = Cl, Br, I)$^{21}$ |
| $(MX_3)_2BBB$ | terpy | $TlCl_3$,$^{a,13}$ $TlBr_3$,$^{a,23}$ $TlI_3$$^{c,13}$ |
| $MX_3 \cdot BBB^d$ | terpy | $GaX_3$ (X = Cl, Br, I),$^{a,24}$ $InX_3$ (X = Cl, Br, I)$^{a,24,25}$<br>$TlX_3$ (X = Cl, Br, I)$^{a,13,21,23,24}$ |
| $MX_3 \cdot 2BBB$ | terpy | $InX_3$ (X = Cl, Br, I)$^{21}$ |

[a] Adducts formed in acetonitrile. [b] BB = 2,9-dimethyl-1,10-phenanthroline. [c] Iodide complex formed from reaction of chloride adduct with NaI. [d] 1:1 adducts of $AlX_3 \cdot$terpy (X = Cl, Br) have been prepared in acetonitrile.[24]

of $AlX_3$ (X = Cl, Br, I) with terpy at a 1:2 mole ratio in acetonitrile. The adduct $AlCl_3 \cdot$terpy is white; $AlBr_3 \cdot 2$terpy, yellow; and $AlI_3 \cdot 2$terpy, red-brown.

The nature of these adducts was deduced from ultraviolet, infrared, and conductivity data.

**Infrared Spectra.** It has been shown that when bpy and phen are complexed to a metal ion, the infrared stretching frequencies of the ligands are shifted to higher frequency, particularly in the regions 1400–1650 cm$^{-1}$ (C=C and C=N ring stretching vibrations) and 725–850 cm$^{-1}$ (C—H out of plane deformations).[5] An unassigned band at 405 cm$^{-1}$ in both bpy and phen adducts also shifts to higher frequencies.

Table II compares the infrared stretching frequencies of the complexes with those of the free base in these three regions. The infrared stretching frequencies observed by Crawford and Melson for the complexes $ScCl_3 \cdot 2$bpy and $ScCl_3 \cdot 2$phen are given in footnote 4. A shift to higher frequencies in the infrared spectra of the aluminum halide complexes is observed in all cases, suggesting bidentate chelation to the metal.

If it is assumed that the C=C, C=N stretching vibrations and the C—H out of plane bending vibrations for terpy absorb at about the same frequency as for bpy and phen, it is possible to demonstrate shifts to higher frequency with tridentate chelation of terpy to the metal. Table II includes the absorptions of free 2,2′,2″-terpyridine in these regions as well as those of the complexes. Shifts to higher frequency are observed in all cases.

**Ultraviolet Spectra and Conductivity Measurements.** Ultraviolet spectra of adducts were measured at various base:acid ratios in acetonitrile. Absorption maxima are listed in Table III. 2,2′-Bipyridine appears to exist in a trans-planar conformation in inert organic solvents[26,27] and exhibits a characteristic $\lambda_{max}$ at 237 and 280 nm. These bands exhibit a shift to 240 and 300–310 nm, respectively, when the base is coordinated to a metal center.[26,28] In solutions of $AlX_3$ and bpy, bidentate chelation is suggested by the observed data. terpy also exhibits a similar bathochromic shift on chelation.[26]

Solutions of $AlX_3$ in acetonitrile are highly conducting and the values obtained during this study and for $AlX_3$ solutions containing added base are given in Table III. Except for $AlI_3$, conductance values increase with added base. Although more than one cationic species could be generated in the $AlX_3$–base solutions, it has been shown that for complexes in acetonitrile, conductance ($\Lambda_M$, $10^{-3}$ M solutions) values of 120–160 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ are typical of 1:1 electrolytes (although $\Lambda_M$ values as low as 92 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ have been observed) and 220–300 $\Omega^{-1}$

$cm^2\ mol^{-1}$ of 1:2 electrolytes (values as low as 145 $\Omega^{-1}\ cm^2\ mol^{-1}$ have been reported). Few data are available for 1:3 electrolytes but values ranging from 340 to 420 $\Omega^{-1}\ cm^2\ mol^{-1}$ have been obtained.[29] The values observed for *solutions* prepared from $AlCl_3$ and $AlBr_3$ with 2 mol of bpy and phen and of $AlI_3$ with 3 mol of bidentate and 2 mol of terpy are in the same range as values obtained for $ScCl_3{\cdot}2BB$ (bpy or phen), formulated as the 1:1 electrolyte $[ScCl_2(BB)_2]Cl$, and $Sc(CNS)_3{\cdot}3BB$ which was formulated as the 1:3 electrolyte $[Sc(BB)_3](CNS)_3$.[5] No conductivity data have been reported as yet for comparable adducts of heavier group 3 halides with bpy, phen, or terpy which contain free halide ion as the counterion. Conductance measurements for $[GaX_3{\cdot}phen]_2$ in acetonitrile gave $\Lambda_0$ values of 161, 151, and 144 $\Omega^{-1}\ cm^2\ mol^{-1}$ for the chloride, bromide, and iodide adducts, respectively. These adducts are presumed to contain the ions $[GaX_2(phen)_2][GaX_4]$.[15]

## Summary

The nature of the aluminum species present in solutions of aluminum halides in acetonitrile is a controversial subject. The solutions are highly conducting which suggests ionic species and Raman and NMR experiments support the presence of the $AlCl_4^-$ ion. An NMR experiment appeared to indicate that only a 1:1.5 adduct was present and the cationic species $[Al(MeCN)_6]^{3+}$ was favored. However, $AlX_3{\cdot}2MeCN$ (X = Cl, Br) precipitated upon slow evaporation of saturated solutions of the halide. Raman spectra were interpreted in terms of the species $[Al(MeCN)_6](AlCl_4)_3{\cdot}2MeCN$ for the solid adduct.[30] A recent x-ray crystal structure of $AlCl_3{\cdot}2MeCN$ has shown it to contain the ion $[AlCl(CH_3CN)_5]^{2+}$ and two $AlCl_4^-$ ions, as well as an acetonitrile molecule of solvation per asymmetric unit,[11] and further demonstrates the difficulty of identification of group 3 halide adducts through spectroscopic techniques.[31]

Apparently all Al–X bonds are not displaced by solvent molecules in the cationic species generated in aluminum halide solutions in acetonitrile, and it is probable that all three cationic species $[Al(CH_3CN)_x]^{3+}$, $[AlX(CH_3CN)_{x-1}]^{2+}$, and $[AlX_2(CH_3CN)_{x-2}]^+$ could exist in equilibrium

$$[AlX_3(CH_3CN)_{x-3}] \rightleftharpoons [AlX_2(CH_3CN)_{x-2}]^+ \rightleftharpoons [AlX(CH_3CN)_{x-1}]^{2+} \rightleftharpoons [Al(CH_3CN)_x]^{3+}$$

with both $X^-$ and $AlX_4^-$ counterions. The distribution of both cationic and anionic species should be halide ion and solvent dependent. Our conductance measurements of $10^{-3}$ M solutions of $AlCl_3$ and $AlBr_3$ in $CH_3CN$ gave similar values but that for $AlI_3$ was considerably higher, which may imply displacement of all Al–I bonds by solvent. Successive addition of base to $AlCl_3$ and $AlBr_3$ results in increase in conductance (concentration of $AlX_3$ held constant) which does not increase above a 1:2 acid to base ratio for $AlCl_3$ but continues to rise up to a 1:5 acid to base ratio for $AlBr_3$. Addition of base to $AlI_3/CH_3CN$ does not significantly alter the initial conductance of $AlI_3$. This observation is at least consistent with the formation of $[AlCl_2(BB)_2]^+$ from $AlCl_3$ and $[Al(BB)_3]^{3+}$ from $AlI_3$ in the presence of bpy or phen as well as suggesting the formation of $[Al(BB)_3]^{3+}$ from $AlBr_3$ and excess phen as reflected in the adducts which were isolated. The ease of displacement of Al–X by solvent is that which would be expected from decreasing bond strength from Al–Cl to Al–I. However it is possible that the exclusive formation of $[AlX_2(BB)]X$ (X = Cl, Br) and of $[Al(BB)_3]I_3$ may be a result of precipitation of the least soluble cationic species and thus does not "prove" a predominant solution species.

The solvent dependence of adduct formation has been shown for heavier group 3 halides. For example, $InCl_3{\cdot}3BB$ is formed in aqueous ethanol[21] and $InCl_3{\cdot}1.5BB$ from ethanol[17] or acetonitrile.[25] A similar solvent dependence may also exist in aluminum halide chemistry. It is apparent that several precipitated adducts include solvent molecules of crystallization, particularly those formed in acetonitrile; cf. $AlCl_3{\cdot}2CH_3CN$,[11] $InCl_3{\cdot}1.5phen{\cdot}CH_3CN$,[18] and $GaBr_3{\cdot}2bpy{\cdot}MeCN$[12] as well as $AlCl_3{\cdot}2bpy{\cdot}CH_3CN$.

Although the adducts $MX_3{\cdot}2BB$ have been previously reported for the heavier group 3 halides (Table IX), this study provides the first crystal structure for this type of adduct and demonstrates the existence of free halide ion as a counterion to the commonly encountered $[MX_2(BB)_2]^+$ cation. Although it is probable that $MX_3{\cdot}3BB$ (BB = bpy or phen) and $MX_3{\cdot}2BBB$ (BBB = terpy) contain the ions $[M(BB)_3]^{3+}$ and $[M(BBB)_2]^{3+}$, we have been unable to obtain suitable crystals for an x-ray study.

We are continuing our studies of the reactions of aluminum halides with polydentate ligands as a function of solvent.

**Acknowledgment.** J.Y.C. wishes to thank the Summer Research Fund of the University of Missouri—St. Louis for initial support of this work; P.L.B. thanks the Graduate School of the University of Missouri—St. Louis for a Graduate Fellowship. E.R.C. wishes to thank Professor M. D. Glick and Wayne State University for facilities and space during sabbatical leave.

**Registry No.** $AlCl_3{\cdot}2bpy{\cdot}CH_3CN$, 61247-59-4; $AlBr_3{\cdot}2bpy$, 36514-98-4; $AlI_3{\cdot}3bpy$, 36514-99-5; $AlCl_3{\cdot}2phen$, 61202-68-4; $AlBr_3{\cdot}2phen$, 61202-69-5; $AlBr_3{\cdot}3phen$, 61202-70-8; $AlI_3{\cdot}3phen$, 61202-71-9; $AlCl_3{\cdot}terpy$, 35935-08-1; $AlBr_3{\cdot}2terpy$, 61202-72-0; $AlI_3{\cdot}2terpy$, 61247-60-7; $AlBr_3{\cdot}3bipy$, 61202-73-1; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; $AlI_3$, 7784-23-8.

**Supplementary Material Available:** Listings of observed and calculated structure factors, hydrogen atom positional and thermal parameters, and least-squares planes of the pyridine rings (12 pages). Ordering information is given on any current masthead page.

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# Crystal and Molecular Structure of Pyridine and 3-Methylpyridine Adducts of [*N,N*-Bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diaminato]cobalt(II) and -nickel(II)

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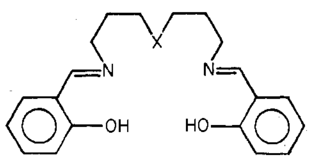
*Received September 7, 1976* AIC60659N

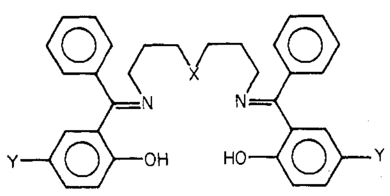
Complexes of *N,N*-bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diamine ($cbpSH_2$) and 3-methylpyridine (mpy) or pyridine (py) with cobalt(II) and nickel(II), [Co(cbpS)mpy], [Ni(cbpS)mpy], and [Ni(cbpS)py], have been synthesized and studied by single-crystal x-ray diffraction. In each case the metal complexes were found to consist of distorted octahedra, with the pentadentate ligand forming a square pyramid about the metal atom, having approximately linear N–M–N′ and O–M–O′ arrangements. The Lewis base mpy or py occupies the sixth octahedral position, opposite the sulfur atom. The metal–thioether bond is of special interest, and in each case this is found to be a normal metal–sulfur bond (Ni, 2.484 (1) Å; Co, 2.537 (1) Å). Although the formation of this bond, especially in the cobalt(II) complex, is unexpected from earlier literature data, it is proposed that such bonds are not the exception but the rule. Each of the three complexes contains a small amount of solvent included in the crystal lattice and the solvent molecules could not be fully located due to extreme positional disorder. No unsolvated complexes were obtained in crystalline form. Crystal data for [Co(cbpS)mpy]: space group $P2_1/c$, $Z = 4$, $a = 16.456$ (7) Å, $b = 14.74$ (1) Å, $c = 16.56$ (1) Å, $\beta = 112.79$ (5)°, $V = 3704$ Å$^3$, $R = 3.7\%$, 2825 reflections. Crystal data for [Ni(cbpS)mpy]: space group $P2_1/c$, $Z = 4$, $a = 16.450$ (6) Å, $b = 14.674$ (1) Å, $c = 16.59$ (1) Å, $\beta = 112.56$ (3)°, $V = 3698$ Å$^3$, $R = 3.7\%$, 2103 reflections. Crystal data for [Ni(cbpS)py]: space group $P2_1/c$, $Z = 4$, $a = 18.002$ (9) Å, $b = 15.691$ (4) Å, $c = 16.401$ (9) Å, $\beta = 116.07$ (4)°, $V = 4164$ Å$^3$, $R = 4.6\%$, 4466 reflections.

## Introduction

Complexes of the potentially pentadentate ligands salX (**1**), cbpX (**2**), and mbpX (X = N, O, S, P) with the metals Cu, Ni, Zn, and Mn have been investigated by a variety of physical techniques.[2-7] Single-crystal x-ray diffraction data have shown that an M–X bond is formed, and hence the ligands act as pentadentates, when X = N,[2,3,6,7] the M–N bond being a normal single bond for M = Zn[7] and Ni[2,3,6] and a dramatically elongated bond for M = Cu.[6] Other physical methods had failed to demonstrate the existence of such a Cu–N bond. Moreover, the results of earlier physical measurements suggest that the M–X bonds are nonexistent or very weak when M–X represents such combinations as $Co^{II}$–S and $Cu^{II}$–S. We will not only demonstrate the formation of M–S bonds for M = Ni(II) and Co(II) with cbpS but also show that the bonds are normal rather than very weak. We further propose that this is not an abnormal but a usual occurrence for such ligands.



**1**, $SalXH_2$



**2**, $cbpXH_2$ (Y = Cl), $mbpXH_2$ (Y = $CH_3$)

We present here the crystal and molecular structures of three complexes with the thioether ligand *N,N*-bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diamine, $cbpSH_2$ (**2**, X = S), and 3-methylpyridine (mpy) or pyridine (py): [Co(cbpS)mpy], [Ni(cbpS)mpy], and [Ni(cbpS)py].

## Experimental Section

The thioether ligand $cbpSH_2$ was prepared as described elsewhere.[8]

**Preparation of the Complexes. [Co(cbpS)] and [Ni(cbpS)].** A solution of the Schiff base ligand $cbpSH_2$ (2 mmol) in 1,1-dimethoxypropane was added to a hot methanol solution of the metal acetate. Piperidine (5 ml) was then added to the solution and the volume reduced until the complex precipitated. Anal. Calcd (Co) for $CoCl_2SO_2N_2C_{32}H_{28}$: C, 60.58; H, 4.45; N, 4.42. Found: C, 60.48; H, 4.42; N, 4.43. Anal. Calcd (Ni) for $NiCl_2SO_2N_2C_{32}H_{28}$: C, 60.60; H, 4.45; N, 4.42. Found: C, 60.55; H, 4.64; N, 4.34.

**[Co(cbpS)mpy](mpy)$_{1/2}$** was prepared by recrystallization of [Co(cbpS)] from hot 3-methylpyridine. Anal. Calcd for $CoCl_2SO_2N_{3.5}C_{41}H_{38.5}$: C, 63.62; H, 5.01; N, 6.33. Found: C, 63.60; H, 5.02; N, 6.28.

**[Ni(cbpS)mpy](mpy)$_{1/2}$** was prepared as above. Anal. Calcd for $NiCl_2SO_2N_{3.5}C_{41}H_{38.5}$: C, 63.62; H, 5.01; N, 6.33. Found: C, 63.96; H, 5.06; N, 6.33.

**[Ni(cbpS)py]·*m*-xylene** was prepared as above, from pyridine solution. The complex was then recrystallized from *m*-xylene. Anal. Calcd for $NiCl_2SO_2N_3C_{45}H_{43}$: C, 65.95; H, 5.28; N, 5.13. Found: C, 66.34; H, 5.38; N, 5.19. For brevity, the included (uncoordinated) solvent molecules will hereafter be omitted from the compound names.

Crystal densities were measured by flotation in aqueous potassium iodide containing detergent as wetting agent.

**Crystal Data for [Co(cbpS)mpy].** $CoCl_2SO_2N_{3.5}C_{41}H_{38.5}$: mol wt 727, space group $P2_1/n$, $Z = 4$, $a = 16.456$ (7) Å, $b = 14.74$ (1) Å, $c = 16.56$ (1) Å, $\beta = 112.79$ (5)°, $V = 3704$ Å$^3$, $d_{calcd} = 1.32$ g cm$^{-3}$, $d_{obsd} = 1.30$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 7.3 cm$^{-1}$; crystal dimensions (distances in mm of faces from centroid) $(11\bar{1})$ 0.07, $(1\bar{1}\bar{1})$ 0.07, (110) 0.08, $(\bar{1}\bar{1}0)$ 0.08, $(1\bar{1}0)$ 0.08, $(\bar{1}10)$ 0.08; red crystal; maximum and