18. *Metallic Complexes of Dimethyl-*o*-methylthiophenylarsine. Part III.*[1] *Complexes of Bivalent Cobalt.*

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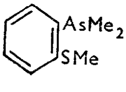
The complexes of dimethyl-*o*-methylthiophenylarsine (As–S) with bivalent cobalt are described. Magnetic susceptibility measurements indicate that the compounds, $[Co(As\text{–}S)_2](ClO_4)_2$ and $[Co(As\text{–}S)_2][CoX_4]$ (X = Cl, Br, I), contain a cation with a square-planar configuration about the cobalt atom, and that the thiocyanato-complex, $[Co(As\text{–}S)(SCN)_2]$, is also square-planar, while the iodo-complex, $[Co(As\text{–}S)_2I_2],2H_2O$, is octahedral. The magnetic susceptibilities of the complexes, $[NR_4]_2[CoX_4]$ (where R = Me, X = Cl; and where R = Et, X = Br, I, SCN), are given also.

In Parts I and II the complexes of nickel and palladium,[2] and copper, silver, and gold,[1] with the ligand dimethyl-*o*-methylthiophenylarsine (I) have been described. This paper reports the compounds formed by bivalent cobalt with this ligand.



(I)

The stereochemical arrangement of bivalent cobalt in complexes can often be inferred from the magnetic moment. Table 1 lists the predicted and observed values for the magnetic moment of bivalent cobalt having square-planar, tetrahedral, octahedral, and tetragonal configurations, severally. Whereas the magnetic moments of other elements of the first transition series are reduced to nearly the spin-only value owing to quenching of the orbital contribution by the electrical field of the surrounding atoms,[3] yet for bivalent cobalt the observed values of the magnetic moment (μ in Bohr magnetons) in a large number of complexes are considerably in excesss of the spin-only value and approach that given by the expression $\mu = \sqrt{[L(L+1) + 4S(S+1)]}$.

Table 1. *Magnetic properties of compounds of bivalent cobalt.*

Stereochemistry	Bonding orbitals	Type of bonding	No. of unpaired electrons	Moment calc. from: $\sqrt{[L(L+1)}$ $+ 4S(S+1)]$		μ (B.M.) (obs.)[4]
					$\sqrt{[4S(S+1)]}$	
Square-planar	$3d4s4p^2$	Spin-paired	1	3·00	1·73	2·1—2·9
Tetrahedral	$4s4p^3$	Spin-free	3	5·21	3·87	4·3—4·8
Octahedral	$4s4p^34d^2$	Spin-free	3	5·21	3·87	4·8—5·3
Sexicovalent (presumably tetragonal) [5, 6]	$3d4s4p^34d$	Spin-paired	1	3·00	1·73	1·7—2·0

An alcoholic solution of cobalt perchlorate, when treated with the arsine (I), yields the perchlorate, $[Co(As\text{–}S)_2](ClO_4)_2,4H_2O$, which has the conductivity expected of a bi-univalent electrolyte in nitrobenzene. The magnetic moment (2·62 Bohr magnetons) corresponds to one unpaired electron (see Table 1), indicating a " spin-paired " square-planar configuration for the cobalt atom, involving $3d4s4p^2$ hybrid bonds. The atoms bonded to cobalt in the cation of this compound are sulphur and arsenic, which have relatively low electronegativities, *viz.*, 2·5 and 2·0, respectively.[7] Ligands with donor atoms of low electronegativity favour spin-pairing, giving rise to square-planar complexes of bivalent nickel and cobalt.[8]

The reaction of cobalt halides with the arsine (I) in alcoholic solution yields crystalline

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[1] Part II, Chiswell and Livingstone, *J.*, 1959, 2931.
[2] Part I, Livingstone, *J.*, 1958, 4222.
[3] Nyholm, *Quart. Rev.*, 1953, **7**, 377.
[4] Figgis and Nyholm, *J.*, 1954, 12.
[5] *Idem*, *J.*, 1959, 338.
[6] For a discussion on deviations from holoedric octahedral symmetry see Jörgensen, Report to the Xth Solvay Council, " Absorption Spectra of Complexes with Unfilled *d*-Shells," Brussels, 1956, p. 16.
[7] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 2nd edn., 1945, p. 60.
[8] Livingstone, *J.*, 1956, 1042.

compounds of empirical formula $Co(As\text{–}S)X_2$ (X = Cl, Br, I). The magnetic moments per cobalt atom vary from 3·86 to 3·98 B.M. If the cobalt atom in these compounds has a planar configuration, the magnetic moment would be within the range 2·1—2·9 B.M., corresponding to one unpaired electron. If, on the other hand, the cobalt atom has a " spin-free " tetrahedral configuration, the moment would be expected to lie within the range 4·3—4·8 B.M., corresponding to three unpaired electrons with the high orbital contribution always found with " spin-free " cobalt(II) complexes.[3] Since the observed magnetic moments do not compare with either of these values, the compounds might better be formulated as salts, $[Co(As\text{–}S)_2][CoX_4]$. If the value of 2·62 Bohr magnetons is accepted for the magnetic moment of the cobalt atom in the cation, as found for the perchlorate, $[Co(As\text{–}S)_2](ClO_4)_2$, the moment of the cobalt atom in the anion can be calculated from the molar susceptibility (χ_M). These values (Table 2) vary from 4·80 to 4·96 B.M. and agree fairly well with the moments of these anions in other compounds. The magnetic moments of cobalt in the compounds $(pyH)_2[CoCl_4]$ and $(pyH)_2[CoBr_4]$ (py = pyridine) have been reported as 4·74 and 4·67 B.M., respectively.[3] The compounds $[NR_4]_2[CoX_4]$ (R = Me, X = Cl; and R = Et, X = Br, I, SCN) were prepared and their magnetic susceptibilities were measured (Table 3). The moments of certain other complexes containing the anion $[CoX_4]^{2-}$ (X = Cl, Br, I) have been found to lie between 4·7 and 4·9 B.M.[9] The tetrahedral structure of the $[CoX_4]^{2-}$ ion (X = Cl, Br) has been established in the compounds Cs_2CoCl_4 and Cs_2CoBr_4,[10] and there seems little doubt that the halogeno-complexes of the arsine (I) contain the tetrahedral anion $[CoX_4]^{2-}$, involving the use of $4s4p^3$ bonding.

TABLE 2. *Molecular conductivities and magnetic susceptibilities of cobalt complexes of dimethyl-*o*-methylthiophenylarsine.*

Compound	Colour	Λ_{2500} in $PhNO_2$ at 25° (mho)	$10^6\chi_M$ at 298°K (corr. for diamagnetism)	μ per Co atom (B.M.)	μ for Co: in cation	in anion
$[Co(As\text{–}S)_2](ClO_4)_2,4H_2O$	Brown	56·3	2860	2·62	2·62	—
$[Co(As\text{–}S)_2][CoCl_4],H_2O$	Green	28·3	12,450	3·88	2·62	4·81
$[Co(As\text{–}S)_2][CoBr_4]$	Bright green	21·5	12,420	3·86	2·62	4·80
$[Co(As\text{–}S)_2][CoI_4]$	Purple	19·7	13,150	3·98	2·62	4·96
$[Co(As\text{–}S)(SCN)_2]$	Greenish-black	7·2	2160	2·28	—	—
$[Co(As\text{–}S)_2I_2],2H_2O$	Blue	3·1	11,800	5·31	—	—

TABLE 3. *Molecular conductivities and magnetic susceptibilities of some* $[CoX_4]^{2-}$ *complexes.*

Compound	Colour	Λ_{1000} in $PhNO_2$ at 25° (mho)	$10^6\chi_M$ at 298°K (corr. for diamagnetism)	μ per Co atom (B.M.
$[NMe_4]_2[CoCl_4]$	Blue	Insol.	9340	4·74
$[NEt_4]_2[CoBr_4]$	Blue	48·7	9560	4·80
$[NEt_4]_2[CoI_4]$	Bright green	54·2	10,060	4·90
$[NEt_4]_2[Co(SCN)_4]$	Deep blue	55·4	8720	4·58

The conductivities of these halogeno-complexes in nitrobenzene (see Table 2) are less than expected for bi-bivalent electrolytes. Their molecular conductances are not markedly increased on further dilution. A possible explanation for the low conductivities is that the compounds exist in the ionic form in the solid state but in nitrobenzene the ionic form is in equilibrium with two molecules of non-electrolyte:

$$[Co(As\text{–}S)_2][CoX_4] \rightleftharpoons 2[Co(As\text{–}S)X_2]$$

The equilibrium lies more in favour of the non-electolyte as the atomic weight of X increases (Cl ⟶ I). It does not appreciably alter with temperature. The variation with temperature of the molecular conductivity in nitrobenzene of the compound $[Co(As\text{–}S)_2][CoBr_4]$

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[9] Harris and Lockyer, personal communication.

[10] Porai-Koshits, *Trudy Inst. Krist. Akad. Nauk S.S.S.R.*, 1954, **10**, 117.

is shown in Fig. 1. The conductivities of two other compounds are given for comparison.

Further evidence of this equilibrium was obtained from spectral measurements in nitrobenzene (see Fig. 2). The complex $[Co(As\text{–}S)_2][CoBr_4]$ displays three absorption maxima at 668, 700, and 724 mμ, respectively, but each maximum has a smaller value for the molar extinction coefficient (ε) than the values of the three peaks at these wavelengths displayed by the compound $[NEt_4]_2[CoBr_4]$. This is in agreement with the equilibrium postulated above. The strong absorption below 475 mμ is also exhibited by the perchlorate, $[Co(As\text{–}S)_2](ClO_4)_2$, but solutions of this compound in nitrobenzene and alcohol do not obey Beer's law, owing to some decomposition in solution with time.

FIG. 1. *Molecular conductivities* (Λ) *in nitrobenzene*: *A*, 1·11 × 10^{-3}M-$[Co(As\text{–}S)_2][CoBr_4]$; *B*, 1·05 × 10^{-3}M-$[AsPh_3Me]I$; *C*, 1·24 × 10^{-3}M-$[NPhMe_3]I$.

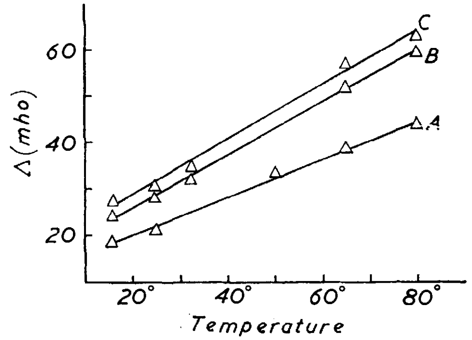


FIG. 2. *Absorption spectra in nitrobenzene solution*: I, $[NEt_4]_2[CoBr_4]$; II, $[Co(As\text{–}S)_2][CoBr_4]$.

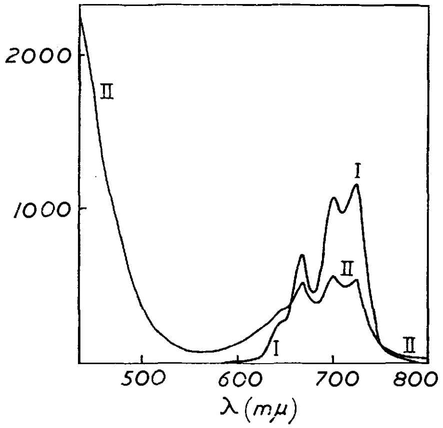
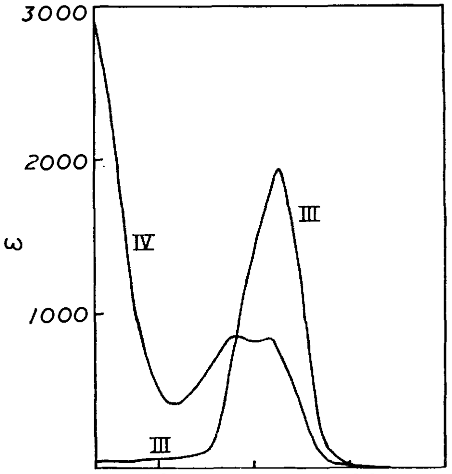


FIG. 3. *Absorption spectra in nitrobenzene solution*: III, $[NEt_4]_2[Co(SCN)_4]$; IV, $Co(As\text{–}S)(SCN)_2$.



A complex of a different type is obtained by reaction of dimethyl-*o*-methylthiophenylarsine with cobalt chloride and ammonium thiocyanate in alcoholic solution. The resulting compound, $Co(As\text{–}S)(SCN)_2$, has a moment of 2·28 B.M., which is consistent with a " spin-paired " square-planar complex. However, on the magnetic data alone a polymeric sexicovalent tetragonal structure with bridging thiocyanato-groups cannot be excluded. Consequently, the infrared absorption spectra of this compound and the complex

$[NEt_4]_2[Co(SCN)_4]$ were examined to obtain any evidence of bridging by thiocyanato-groups in the former complex. Co(As–S)$(SCN)_2$ has a thiocyanato-stretching frequency at 2063; and $[NEt_4]_2[Co(SCN)_4]$ one at 2056 cm.$^{-1}$. For a number of thiocyanato-complexes of bivalent palladium and platinum it has been shown[11] that those complexes which contain bridging thiocyanato-groups display an absorption maximum at 2154—2182 cm.$^{-1}$, while those in which the thiocyanato-group is terminal have maxima in the range 2105—2120 cm.$^{-1}$. Silver thiocyanate, which contains bridging thiocyanato-groups,[12] has a maximum at 2149 cm.$^{-1}$.[13] The infrared data indicate that there are no bridging thiocyanato-groups in the compound Co(As–S)$(SCN)_2$ and exclude a polymeric structure, since, for a given metal, bridging thiocyanato-groups display a maximum at a frequency some 30—60 cm.$^{-1}$ higher than the frequency of a terminal thiocyanato-group.[14]

The small conductivity of the complex in nitrobenzene could be due to a small amount of rearrangement in solution to the ionic form, $[Co(As–S)_2][Co(SCN)_4]$. We endeavoured to obtain evidence for this rearrangement from spectral measurements (Fig. 3). The complex $[NEt_4]_2[Co(SCN)_4]$ has a strong absorption maximum at 627 mμ. The complex Co(As–S)$(SCN)_2$ displays a broad absorption band in the region of 600 mμ with two peaks at 583 and 618 mμ, and also strong absorption below 475 mμ. This evidence is not conclusive, but is not inconsistent with the hypothesis that in nitrobenzene solution the compound is in equilibrium with the salt $[Co(As–S)_2][Co(SCN)_4]$.

A third type of cobalt complex was obtained with the same ligand. The blue iodo-complex, $Co(As–S)_2I_2,2H_2O$, has a moment of 5·31 B.M. In this the cobalt atom is " spin-free " with an octahedral configuration, using $4s4p^34d^2$ bonding orbitals. In this regard the compound is analogous to the nickel complex, $Ni(As–S)_2I_2$, which is " spin-free " with a moment corresponding to two unpaired electrons.[2] On the other hand, it differs from the " spin-paired " cobalt complex of *o*-phenylenebisdimethylarsine (As–As), $Co(As–As)_2I_2$, which has a moment of 2·4 B.M.[15]

EXPERIMENTAL

*Bisdimethyl-*o*-methylthiophenylarsinecobalt*(II) *Perchlorate Tetrahydrate*.—A solution of cobalt perchlorate hexahydrate (0·4 g.) and dimethyl-*o*-methylthiophenylarsine (0·5 g.) in alcohol (10 ml.) was evaporated to 2—3 ml. to yield brown crystals of the complex *perchlorate* (0·4 g.), which were washed with a few drops of acetone, then with ligroin (Found: C, 27·6; H, 4·6; Co, 7·4; H_2O, 9·2. $C_{18}H_{34}O_{12}Cl_2S_2As_2Co$ requires C, 27·6; H, 4·4; Co, 7·5; H_2O, 9·2%). The water of hydration is lost *in vacuo* over phosphoric oxide, but is rapidly taken up again in moist air.

*Bisdimethyl-*o*-methylthiophenylarsinecobalt*(II) *Tetrachlorocobaltate*(II) *Monohydrate*.—Anhydrous cobalt chloride (0·4 g.) in 95% alcohol (10 ml.) was treated with dimethyl-*o*-methylthiophenylarsine (0·5 g.) in alcohol (10 ml.). The green solution was evaporated to 10 ml. and, on cooling, deposited green crystals of the *compound*, which was recrystallized from alcohol and dried (P_2O_5) (yield, 0·4 g.) (Found: C, 28·5; H, 3·7; Cl, 19·4; Co, 16·2. $C_{18}H_{28}OCl_4S_2As_2Co_2$ requires C, 28·4; H, 3·8; Cl, 19·3; Co, 16·1%).

*Bisdimethyl-*o*-methylthiophenylarsinecobalt*(II) *Tetrabromocobaltate*(II).—The *compound* was prepared from anhydrous cobalt bromide (0·5 g.) in the same manner as the chloro-complex. On recrystallization a crop of bright-green crystals (0·3 g.) was obtained (Found: C, 24·3; H, 2·8; Br, 35·4; Co, 13·1. $C_{18}H_{26}Br_4S_2As_2Co_2$ requires C, 24·2; H, 2·9; Br, 35·7; Co, 13·2%).

*Bisdimethyl-*o*-methylthiophenylarsinecobalt*(II) *Tetraiodocobaltate*(II).—Anhydrous cobalt iodide (0·7 g.) in alcohol (20 ml.) was treated with a solution of dimethyl-*o*-methylthiophenylarsine (0·5 g.) in alcohol (10 ml.). The solution was evaporated to 15 ml. and on cooling deposited a small quantity of purple crystals of the *compound*. The preparation was repeated twice in order to obtain a sufficient yield (0·4 g.) (Found: C, 19·9; H, 2·5; Co, 10·8. $C_{18}H_{26}I_4S_2As_2Co_2$ requires C, 20·0; H, 2·4; Co, 10·9%).

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[11] Chatt and Duncanson, *Nature*, 1956, **178**, 997.

[12] Lindqvist, *Acta Cryst.*, 1957, **10**, 29.

[13] Chatt, Duncanson, Hart, and Owston, *Nature*, 1958, **181**, 43.

[14] Gatehouse, personal communication.

[15] Nyholm, *J.*, 1950, 2071.

*Dithiocyanatodimethyl-*o*-methylthiophenylarsinecobalt*(II).—Anhydrous cobalt chloride (0·2 g.) in alcohol (10 ml.) was treated with ammonium thiocyanate (0·3 g.) in alcohol (10 ml.), followed by dimethyl-*o*-methylthiophenylarsine (0·5 g.) in ethyl alcohol (10 ml.). After a few minutes, the black solution deposited greenish-black crystals of the solvated *complex*, which was filtered off and dried (P_2O_5) (yield 0·2 g.); the alcohol of solvation is driven off at a temperature above 150° (Found: C, 33·8; H, 3·9; N, 7·1; Co, 13·9. $C_{11}H_{13}N_2S_3AsCo,\frac{1}{2}C_2H_5{\cdot}OH$ requires C, 33·8; H, 3·8; N, 6·6; Co, 13·8%).

*Di-iodobisdimethyl-*o*-methylthiophenylarsinecobalt*(II) *Dihydrate.*—A warm solution of anhydrous cobalt iodide (0·7 g.) in alcohol (20 ml.) was treated with a solution of dimethyl-*o*-methylthiophenylarsine (0·5 g.) in alcohol (10 ml.). The solution was concentrated to half the original volume and cooled. The crop of purple crystals was filtered off, and the filtrate was further evaporated to give a blue oil, which, when scratched, yielded blue crystals of the *complex* (0·7 g.), which were washed with a small amount of alcohol (Found: C, 26·9; H, 3·3; I, 31·5; Co, 7·5%; *M*, cryoscopically in 0·68% nitrobenzene solution, 665. $C_{18}H_{30}O_2I_2S_2As_2Co$ requires C, 26·8; H, 3·7; I, 31·5; Co, 7·3%; *M*, 805). The water of hydration is not removed *in vacuo* over phosphoric oxide, but is driven off when the compound is heated in a closed tube.

Note. For molecular-weight determinations in nitrobenzene a salt–hydrate pair, sodium sulphate–sodium sulphate decahydrate, was employed as described by Roberts and Bury.[16] Consequently, if a compound contains lattice water, this water will not cause a lowering of the freezing point, and thus will not give an abnormally low value for the molecular weight.

Tetramethylammonium Tetrachlorocobaltate(II).—Anhydrous cobalt chloride (0·52 g.) in alcohol (20 ml.) was treated with a solution of tetramethylammonium chloride (0·66 g.) in alcohol (15 ml.). The light blue precipitate of the *chloro-complex* was filtered off and recrystallized from alcohol (yield, 0·5 g.) (Found: C, 27·5; H, 6·2; N, 8·4; Cl, 39·8. $C_8H_{24}N_2Cl_4Co$ requires C, 27·5; H, 6·9; N, 8·0; Cl, 40·6%).

Tetraethylammonium Tetrabromocobaltate(II).—Anhydrous cobalt bromide (0·43 g.) in alcohol (20 ml.) was treated with tetraethylammonium bromide (0·6 g.) in alcohol (20 ml.). The blue *compound* was filtered off and recrystallized from alcohol (yield, 0·6 g.) (Found: C, 30·2; H, 6·2; N, 4·1; Br, 50·0; Co, 9·1. $C_{16}H_{40}N_2Br_4Co$ requires C, 30·1; H, 6·3; N, 4·4; Br, 50·0; Co, 9·2%).

Tetraethylammonium Tetra-iodocobaltate(II).—The bright green *iodo-complex* was similarly obtained (Found: C, 23·2; H, 4·7; N, 3·1; I, 61·4; Co, 7·3. $C_{16}H_{40}N_2I_4Co$ requires C, 23·2; H, 4·9; N, 3·4; I, 61·4; Co, 7·1%).

Tetraethylammonium Tetrathiocyanatocobaltate(II).—Addition of a solution of tetraethylammonium bromide (0·6 g.) in alcohol (20 ml.) to anhydrous cobalt chloride (0·52 g.) and ammonium thiocyanate (1 g.) in alcohol (20 ml.) gave deep blue crystals of the thiocyanato-complex (0·5 g.) (Found: C, 43·7; H, 7·0; N, 14·8; Co, 10·7. $C_{20}H_{40}N_6S_4Co$ requires C, 43·5; H, 7·3; N, 15·2; Co, 10·7%).

Magnetic Susceptibility.—The magnetic susceptibilities of the cobalt complexes were measured on the solid compounds at room temperature with a balance similar to that described by Baddar, Hilal, and Sugden.[17] The values for the diamagnetic corrections were taken from Selwood.[18]

Infrared Spectra.—These were obtained from Nujol mulls, sodium chloride optics being used.

Visible and Ultraviolet Spectra.—These were measured on solutions of the complexes in nitrobenzene by using a Beckman spectrophotometer.

Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen, of the micro-analytical laboratory of this University.

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[16] Roberts and Bury, *J.*, 1923, **123**, 2037.

[17] Baddar, Hilal, and Sugden, *J.*, 1949, 132.

[18] Selwood, "Magnetochemistry," Interscience Publishers Inc., New York, 1943, p. 52.