515. *Complexes of Bivalent and Tervalent Cobalt with a Terdentate and a Quadridentate Amine.*

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2 : 2′-Diaminodiethylamine (dn) with cobaltous salts yields compounds Co dnX_2 and Co dn$_2$$X_2$; their magnetic moments indicate that no spin-pairing occurs. Both types are readily oxidised to tervalent cobalt complexes, Co dn$_2$$X_3$, which are diamagnetic and, therefore, spin-paired and octahedral. The compound Co dn$(NO_2)_3$ is also spin-paired and octahedral. This behaviour is compared with that of a tritertiary arsine which causes electron-pairing in all cases and forms quinquecovalent complexes with cobaltous halides.

2 : 2′ : 2″-Triaminotriethylamine forms spin-free compounds Co trenX_2 with bivalent cobalt salts. Co tren$(OH)_2Cl$ and Co tren$(SCN)_3,H_2O$ are diamagnetic compounds, indicating the usual spin-paired type complex of tervalent cobalt.

As part of an investigation concerned with the effects of multidentate chelate groups and of the electronegativity of the donor atom on the stereochemistry and bond type of transition-metal complexes, we have studied the compounds of cobalt salts with 2 : 2′-diaminodiethylamine and 2 : 2′ : 2″-triaminotriethylamine. Although a few complexes of these amines [1, 2, 3] have been prepared and the susceptibility of one of them reported,[4] no systematic magnetic studies have been carried out.

Table 1.

Valency	Stereochem.	Bonding orbitals	No. of unpaired electrons	Magnetic moments * Calc.	Found
II	Planar	$3d4s4p^2$	1	1·73	2·1—2·9
II	Octahedral	$3d^24s4p^3$	1 †	1·73	1·7—2·0
II	Tetrahedral	$4s4p^3$	3	3·87	4·3—4·8
II	Octahedral	$4s4p^34d^2$	3	3·87	4·8—5·2
III	Octahedral	$3d^24s4p^3$	0	0·00	Diamagn.
III	Octahedral	$4s4p^34d^2$	4	4·90	4·26

* In Bohr magnetons. The calculated moments are spin-only values. † See below.

Recently the relation between bond type and electronegativity of the donor atom has received much attention.[5, 6] Calculations of overlap integrals for the use of 3*d*- and 4*d*-orbitals by metals of the first transition series support the conclusions that the more electronegative donor atoms should favour the use of octahedral $4s4p^34d^2$-bonding orbitals, while the less electronegative donors should favour $3d^24s4p^3$-orbitals.[7] In the latter case it is generally necessary for electron-pairing to occur in order to free sufficient 3*d*-orbitals for bonding; complexes of this type are therefore known as " spin-paired," but with the former type such electron-pairing is not required and the complexes are " spin-free." [8] This subject has been reviewed from the standpoint of the ligand-field theory.[9] It is therefore of interest to compare the complexes of ligands with donor atoms of high electronegativity, *e.g.*, nitrogen, with those of lower electronegativity, *e.g.*, arsenic.

The relation between the valency states and the stereochemistry of cobalt in its coordination compounds with their magnetic moments is shown in Table 1 (cf. Figgis and

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[1] Breckenridge, *Canad. J. Res.*, 1948, **26**, *B*, 11; Mann and Pope, *J.*, 1926, 483.

[2] Mann, *J.*, 1934, 471.

[3] Mann, *J.*, 1929, 409.

[4] Cox and Webster, *Z. Krist.*, 1935, **92**, 478.

[5] Taube, *Chem. Rev.*, 1952, **50**, 69.

[6] Burstall and Nyholm, *J.*, 1952, 3570.

[7] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332; Craig, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 4.

[8] Nyholm, Reports of the Xth Solvay Council, Brussels, May, 1956.

[9] Griffiths and Orgel, *Quart. Rev.*, 1957, **11**, 381; Gillespie and Nyholm, *ibid.*, p. 339.

Nyholm[10]). With bivalent cobalt the use of the magnetic moment to determine the number of unpaired electrons on the metal atom fails to distinguish between tetrahedral and octahedral complexes of the spin-free type, and between planar and octahedral co-ordination in spin-paired complexes. According to Nyholm,[11] the magnitude of the orbital contribution to the magnetic moment (the amount by which the moment exceeds that calculated from the " spin-only " formula) may be diagnostic of the stereochemistry of the metal. In the case of spin-free complexes of bivalent cobalt, a field of tetrahedral symmetry should cause a greater quenching of the orbital contribution than one of octahedral symmetry. These conclusions are found to be true in practice and from a study of the magnetic moments of a large number of compounds it has been postulated that the moments of tetrahedral complexes are generally lower than 4·8 B.M., while those of octahedral complexes lie in the range 4·8—5·2 B.M.[10, 11]

With spin-paired complexes the conclusions are similar. Planar complexes have one unpaired electron in a $3d$-orbital where there would be expected to be a significant orbital contribution; in agreement, the moments of such compounds are found to lie in the range 2·1—2·9 B.M. (spin-only value 1·73 B.M.). With octahedral complexes the problem is more difficult. If the bonding orbitals are $3d^24s4p^3$ it is necessary to remove one electron († in Table 1) from a $3d$-orbital in order to free two such orbitals for bonding. The most energetically favourable orbital for this electron is now the $5s$, where, since the angular momentum is zero, the orbital contribution should be zero; in fact, the observed moments for such complexes (1·7—2·0 B.M.) lie close to the spin-only value. However, the Referees have kindly pointed out that the alternative view is that the electron remains in the $3dz^2$ orbital, where it would repel two donor atoms in *trans*-positions. This would imply that the bonding orbitals were of two types, *viz.*, $3d4s4p^2$ square planar and two longer $4p4d$ collinear bonds perpendicular to the plane. This view has not been experimentally substantiated for octahedral spin-paired bivalent cobalt complexes, but an X-ray study[12] of [Pd(diarsine)$_2$I$_2$] (where there would be expected to be two electrons in the $4dz^2$ orbital) has shown that the two Pd–I distances are longer than expected for $4d^25s5p^3$-bonding.

TABLE 2. *Magnetic moments of powdered samples at 20°.*

Complex	Colour	$10^6\chi_M$	Diamag.* (corr.)	$10^6\chi'_M$	μ (B.M.)
Co dnCl$_2$	Blue	9390	114	9504	4·74
Co dnBr$_2$	Blue	9140	132	9272	4·68
Co dn$_2$Cl$_2$,H$_2$O	Violet	11,510	194	11,704	5·26
Co dn$_2$Cl$_2$	Violet-blue	11,530	181	11,711	5·26
Co dn$_2$I$_2$	Purple	11,040	236	11,276	5·16
Co dn$_2$(ClO$_4$)$_2$	Purple	9710	199	9909	4·84
Co dn$_2$I$_3$	Brown	—†	—	—	0·00
Co dn$_2$(ClO$_4$)$_3$	Brown	—†	—	—	0·00
Co dn(NO$_2$)$_3$	Yellow-brown	—†	—	—	0·00
Co tren(SCN)$_2$	Olive-green	9520	157	9677	4·78
Co trenI$_2$	Blue	9360	197	9557	4·75
Co tren(OH)$_2$Cl	Brown	—†	—	—	0·00
Co tren(SCN)$_2$SCN,H$_2$O	Red	—†	—	—	0·00

* These values are calculated from constants given by Selwood;[13] the diamagnetism of the metal has been ignored in all cases. † The method of measurement did not permit the precise determination of diamagnetic susceptibilities.

Our experimental results for the complexes of bivalent and tervalent cobalt with 2 : 2′-diaminodiethylamine (dn) and 2 : 2′ : 2″-triaminotriethylamine (tren) are summarised in Table 2. The complexes of bivalent cobalt are very readily oxidised in solution and it is therefore necessary to exclude air during their preparation. Solutions of the ligand and

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[10] Figgis and Nyholm, *J.*, 1954, 12.

[11] Nyholm, *Quart. Rev.*, 1953, **7**, 402; Klyne, " Progress in Stereochemistry," Butterworths London, 1955, p. 333.

[12] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

[13] Selwood, " Magnetochemistry," Interscience Publ. Inc., New York, 1943, p. 52.

cobalt salt in alcohol were mixed and the complex was filtered off in an all-glass apparatus which allowed the whole operation to be carried out in an atmosphere of nitrogen.

The tervalent complexes with both ligands are diamagnetic; hence $3d^24s4p^3$ octahedral orbitals of the metal are probably involved in the bonding. The conductivities in aqueous solution of Co dn_2I_3 (350 mho) and Co $dn_2(ClO_4)_3$ (339 mho) indicate that they are behaving as ter-univalent electrolytes. Unless water molecules are co-ordinated with the ion in solution, the diaminodiethylamine acts as a terdentate ligand in these compounds. Similarly as [Co tren$(SCN)_2$]SCN and [Co tren$(OH)_2$]Cl behave as uni-univalent electrolytes in water, it seems likely that the triaminotriethylamine is bonded to the cobalt atom through each of its four amino-groups. It is assumed, therefore, that the two ligands act as terdentate and quadridentate donors respectively in the other complexes isolated.

The compounds of bivalent cobalt are all of the spin-free type. Those with empirical formula Co dnX_2 may be formulated either as complexes containing tetrahedrally co-ordinated cobalt(II) [Co dnX]X, or as dimeric compounds, [Co dn_2][CoX_4]. Their magnetic moments (4·7 B.M.) do not distinguish between these two structures; the former should have a moment somewhat lower than 4·8 B.M., while the mean moment of the two cobalt atoms in the second formulation should be the mean of the values for Co $dn_2(ClO_4)_2$ (4·84 B.M.) and for $[CoX_4]^{2-}$ (4·76 B.M., X = Cl; 4·62 B.M., X = Br), *viz.*, 4·8 and 4·7 B.M. for the chloride and bromide respectively. The compounds Co dn_2X_2 (X = Cl, I, ClO_4) have magnetic moments in the range 4·8—5·3 B.M. and are probably octahedral complexes involving $4s4p^34d^2$-orbitals of the cobalt atom.

The behaviour of the tri-tertiary arsine, $CH_3{\cdot}As(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsMe_2)_2$ with cobaltous salts[14] forms an interesting contrast with the corresponding compound, diaminodiethylamine, containing donor atoms of greater electronegativity. Thus, the triarsine causes electron-pairing in all cases while the amine fails to do so. In nitrobenzene solution the compounds containing one triarsine group per cobalt atom are non-electrolytes and are probably quinquecovalent, at least in this solvent. The magnetic moments indicate one unpaired electron; hence, the $3d$-orbitals of the cobalt atom are involved in bonding, probably forming $3d4s4p^3$-hybrid orbitals and a square-pyramidal arrangement of ligand atoms. Although the bis(terdentate)cobalt(II) complexes with both ligands are octahedral, the triarsine causes electron-pairing whereas the diaminodiethylamine compounds are of the spin-free type. All these bivalent cobalt compounds are readily oxidised in solution to complexes of tervalent cobalt.

Non-ionic complexes of tervalent cobalt of the type Co(terdentate)X_3 were isolated more easily with the triarsine than with diaminodiethylamine. With the latter, Co $dn(NO_2)_3$ was the only compound of this type obtained. However, while diaminodiethylamine forms the complexes Co dn_2X_3 ($X = I^-$ or ClO_4^-), no similar compound containing two triarsine groups is obtained. Both ligands, in common with practically all others, form diamagnetic complexes of tervalent cobalt which are spin-paired and octahedral.

From the reaction of triaminotriethylamine with cobaltous salts, the compounds Co trenX_2 (X = SCN or I) were the only two isolated. The values of their magnetic moments (4·8 B.M.) do not distinguish between the two possible stereochemical arrangements (tetrahedral or octahedral) but indicate that the complexes are of the spin-free type.

EXPERIMENTAL

Commercial diaminodiethylamine was purified by distillation under reduced pressure (b. p. 93—94°/17 mm.).

2 : 2′-*Diaminodiethylaminecobalt*(II) *Chloride.*—Cobalt chloride hexahydrate (1·0 g.) in air-free absolute alcohol (20 ml.) was treated with diaminodiethylamine (0·5 g.) in air-free absolute alcohol (10 ml.). A blue solid quickly separated from the deep blue solution. The *chloride*

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[14] Barclay and Nyholm, *Chem. and Ind.*, 1953, 378, also unpublished results; cf. Barclay, *Rev. Pure Appl. Chem. (Australia)*. 1954, **4**, 77.

was filtered off under nitrogen, washed with air-free alcohol–ether, and dried in a vacuum-desiccator (Found: C, 20·4; H, 5·6; Cl, 30·2. $C_4H_{13}Cl_2N_3Co$ requires C, 20·6; H, 5·6; Cl, 30·4%). The mol. conductivity in M/1000-aqueous solution at 22° = 197 mho.

Similarly prepared were the analogous salts:

Bromide (1·4 g. from 1·55 g. of cobalt bromide), blue (Found: C, 14·8; H, 4·3; Br, 49·9. $C_4H_{13}Br_2N_3Co$ requires C, 14·9; H, 4·1; Br, 49·6%), mol. conductivity in M/1000-aqueous solution at 22° = 218 mho.

Chloride (1·8 g. from 1·5 g. of cobalt chloride hexahydrate and 1·3 g. of diaminodiethylamine), violet-blue (Found: C, 28·3; H, 7·9; Cl, 21·0. $C_8H_{26}Cl_2N_6Co$ requires C, 28·6; H, 7·8; Cl, 21·1%), mol. conductivity in M/1000-aqueous solution at 24° = 224 mho.

Chloride monohydrate (1·0 g. from 1·5 g. of cobalt chloride hexahydrate), violet (from 90% aqueous alcohol) (Found: C, 27·0; H, 8·2; Cl, 20·0. $C_8H_{28}OCl_2N_6Co$ requires C, 27·1; H, 8·0; Cl, 20·0%), mol. conductivity in M/2000-aqueous solution at 24° = 224 mho.

Iodide, purple (Found: C, 18·3; H, 4·8; I, 48·7. $C_8H_{26}I_2N_6Co$ requires C, 18·5; H, 5·05; I, 48·9%), mol. conductivity in M/1000-aqueous solution at 23° = 229 mho.

Perchlorate (1·2 g. from 1·5 g. of cobalt perchlorate), purple (Found: C, 20·6; H, 5·5. $C_8H_{26}O_8Cl_2N_6Co$ requires C, 20·7; H, 5·65%), mol. conductivity in M/1000-aqueous solution at 22° = 216 mho.

Bis-(2 : 2′*-diaminodiethylamine*)*cobalt*(III) *Iodide*.—The dark brown crystals were prepared by Mann's method [2] (Found: C, 15·3; H, 4·05; I, 59·0. Calc. for $C_8H_{26}I_3N_6Co$: C, 14·9; H, 4·05; I, 58·9%), mol. conductivity in M/2000-aqueous solution at 24° = 350 mho.

Bis-(2 : 2′*-diaminodiethylamine*)*cobalt*(III) *Perchlorate*.—The solution containing the $[Co\ dn_2]^{3+}$ ion, prepared from aquopentamminocobalt(III) chloride (4·0 g.) by Mann's method,[2] was poured into a concentrated solution of sodium perchlorate; deep brown crystals of the *perchlorate* were deposited slowly. The complex (2·9 g.) was recrystallised from water (Found: C, 17·0; H, 4·8. $C_8H_{26}O_{12}Cl_3N_6Co$ requires C, 17·05; H, 4·6%) and had mol. conductivity in M/1000-aqueous solution at 23° = 339 mho.

Trinitro-(2 : 2′*-diaminodiethylamine*)*cobalt*(III).—This compound was prepared after attempts to obtain complexes of the type $Co\ dnX_3$ (X = Cl, Br, or SCN) had failed. Diaminodiethylamine (7·6 g.) and sodium nitrite (80·0 g.) were dissolved in water (250 ml.), and a solution of cobaltous acetate (18·3 g.) in water (100 ml.) was added. To the ice-cold mixture, hydrogen peroxide (20-vol.; 15 ml.) was added with stirring. The red solution became brown and a yellow-brown solid separated overnight. This mixture was heated with decolorising charcoal and filtered. A solid (5·0 g.) then crystallised at 0°, and was recrystallised from a large volume of hot water containing a few drops of acetic acid. The *complex* (3·5 g.) separated as yellow-brown plates which were moderately soluble in hot water but insoluble in organic solvents (Found: C, 16·1; H, 4·35. $C_4H_{13}O_6N_6Co$ requires C, 16·0; H, 4·4%), mol. conductivity in M/2000-aqueous solution at 23° = 28 mho.

2 : 2′ : 2″*-Triaminotriethylamine Trihydrochloride*.—The colourless crystals, prepared by the method of Mann and Pope,[15] were purified by recrystallisation from aqueous alcohol.

2 : 2′ : 2″*-Triaminotriethylaminecobalt*(II) *Thiocyanate*.—Triaminotriethylamine trihydrochloride (0·6 g.) was warmed with 33% sodium hydroxide solution (0·75 ml.) on a water-bath. Absolute alcohol (40 ml.) was added and the precipitated sodium chloride filtered off. The solution was de-aerated by boiling, then added to a solution of cobaltous thiocyanate (0·4 g.) in air-free absolute alcohol (20 ml.). The mixture, which was kept under nitrogen, became green and an olive-green precipitate was formed. The *complex* (0·6 g.) was filtered off quickly, washed with alcohol–ether, and dried in a vacuum-desiccator (Found: C, 30·0; H, 5·4. $C_8H_{18}N_6S_2Co$ requires C, 29·9; H, 5·65%).

2 : 2′ : 2″*-Triaminotriethylaminecobalt*(II) *Iodide*.—By reaction as for the thiocyanate, triaminotriethylamine trihydrochloride (0·4 g.) gave the *iodide* (0·5 g.) as a blue solid (Found: C, 15·6; H, 3·75. $C_6H_{18}I_2N_4Co$ requires C, 15·7; H, 3·95%).

Dihydroxy-(2 : 2′ : 2″*-triaminotriethylamine*)*cobalt*(III) *Chloride*.—Triaminotriethylamine trihydrochloride (0·4 g.) was dissolved in 33% sodium hydroxide solution (0·6 ml.), diluted with water (20 ml.), and warmed on the steam-bath. This solution was added to cobalt chloride hexahydrate (0·4 g.) in water (25 ml.), and filtered air was bubbled through the mixture for 24 hr. The resulting deep crimson solution was poured into a large volume of alcohol, crystals

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[15] Mann and Pope, *Proc. Roy. Soc.*, 1925, **109**, *A*, 444.

being slowly deposited. The *complex* (0·4 g.) was filtered off, washed with alcohol, and air-dried (Found: C, 26·0; H, 7·4; Cl, 12·8. $C_6H_{20}O_2ClN_4Co$ requires C, 26·2; H, 7·3; Cl, 12·9%). It had mol. conductivity in M/1000-aqueous solution at 22° = 142 mho.

Dithiocyanato-(2 : 2′ : 2″-triaminotriethylamine)cobalt(III) *Thiocyanate Monohydrate.*—The brilliant red needles, prepared by Mann's method,[3] were recrystallised twice from a small volume of hot water (Found: C, 27·6; H, 5·1. Calc. for $C_9H_{20}ON_7S_3Co$: C, 27·4; H, 5·05%), mol. conductivity in M/2000-aqueous solution at 22° = 121 mho.

Magnetic Measurements.—The magnetic susceptibilities were determined on the finely powdered solids (*ca.* 10 mg.) in an apparatus of the type described by Blaha.[16] The sensitivity of the microbalance was such as to permit accurate determination of paramagnetic susceptibilities, though the smaller diamagnetic susceptibility of the complexes of tervalent cobalt could not be measured precisely.

Conductivity Measurements.—A conductance bridge with a dip-type cell was used.

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[16] Blaha, *Mikrochemie*, 1952, **39**, 339.