

Magnetic Moments and Stereochemistry of Cobaltous Compounds.

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[Reprint Order No. 4463.]

The orbital contributions to the magnetic moments of four- and six-covalent cobaltous compounds when the binding is (i) "ionic" and (ii) "covalent" are compared. In the first case, in which no electron pairing occurs, it is well established that the orbital contribution is smaller in the four-covalent (tetrahedral) complexes than in those which are six-covalent (octahedral). When electron pairing occurs, however, it is found experimentally that the orbital contribution is much larger in the four-covalent (square planar) molecules. The small orbital contribution in octahedral "covalent" molecules can be understood on the Pauling theory if promotion of the electron to a 5s orbital is accepted, but the theoretical interpretation of the square planar case is more difficult. The possible use of the relative sizes of the orbital contributions as a diagnostic tool in inorganic stereochemistry is discussed.

THE magnetic moments (μ) of bivalent cobalt compounds fall into two classes. In the first, the so-called "ionic" complexes, μ lies in the range 4.3—5.6 B.M., whilst, in the second, much smaller values (1.8—2.9 B.M.) are observed. In the ground state (${}^4F_{3/2}$) the Co^{++} ion contains three unpaired 3d electrons (cf. Table 1), and if the magnetic moment is calculated on the "spin only" formula, $\mu = \sqrt{4S(S+1)}$, a value of 3.88 B.M. is expected. It is generally assumed (Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 2nd Edn., 1940, p. 112; Nyholm, *Quart. Reviews*, 1953, 7, 377) that the first class of moments arise from the presence of so-called "ionic" or "higher-level covalent bonds" (cf. Taube, *Chem. Reviews*, 1952, 50, 69; Burstall and Nyholm, *J.*, 1952, 3570), the three unpaired electrons of the Co^{++} ion remaining uncoupled. The higher-level covalent bonds expected are $4s4p^3$ (tetrahedral) in a four-covalent complex and $4s4p^34d^2$ (octahedral) when the complex is six-covalent. The excess over the "spin only" value of 3.88 B.M. is attributed to incomplete quenching of the orbital contribution which has the value $L(L+1)$ in the expression $\mu = \sqrt{L(L+1) + 4S(S+1)}$. The smaller moments observed in the second class of compound are taken to indicate electron pairing owing to the formation of strong covalent bonds using one or two of the 3d orbitals of the Co(II) atom, *i.e.*, $3d4s4p^2$ square or $3d^24s4p^3$ octahedral complexes respectively. As with the "ionic" compounds, the orbital contribution in excess of the "spin only" value for one unpaired electron (1.73 B.M.) varies from one compound to another.

The relation between stereochemistry and orbital contribution in "ionic" compounds has been established on a sound theoretical basis and the conclusions are consistent with experimental results (for detailed references see Nyholm, *loc. cit.*) Briefly, when the Co^{++} ion, which is in an F spectroscopic state, is surrounded by four ligands at the corners of a tetrahedron the resulting negative cubic crystalline field constant gives rise to a Stark pattern composed of a lowest-lying single state separated from two triply degenerate levels by energy intervals $\gg kT$. As a result the level almost exclusively occupied is

the lowest-lying singlet. This causes the metal atom to behave very much as though it were in an *S* state, for which the orbital contribution is zero. In octahedral "ionic" complexes, however, the cubic crystalline field constant is positive; this causes an inversion of the Stark pattern observed for the negative field constant and the triplet is now the lowest-lying

TABLE 1. Stereochemistry of cobaltous compounds.

Type of binding	Electronic arrangement				Stereo-chemistry and bond orbitals	Range of magnetic moment (B.M.)
	3d	4s	4p	4d		
Free Co ⁺⁺ ion	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$		
"Ionic" or "higher-level" covalent bonds	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	Tetrahedral 4s4p ³	4.3—4.8
"Lower-level" covalent bonds	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	Octahedral 4s4p ³ 4d ²	4.9—5.6
"Lower-level" covalent bonds	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$		Square planar 3d4s4p ²	2.1—2.9
	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	5s $\uparrow\downarrow$	Octahedral 3d ² 4s4p ³	1.7—2.0

TABLE 2. Magnetic moments of cobaltous compounds.

Octahedral complexes			Square complexes		
Substance	Moment	Ref.	Substance	Moment	Ref.
[Co(NO ₂) ₆] ⁴⁻ ion (compounds with different cations) :	1.8—1.9	1	K ₂ bisoxamide Co(II)	2.91	7
K ₂ Ca[Co(NO ₂) ₆]	1.83	2	K ₂ bismalonamide Co(II)	2.70	7
K ₂ Pb[Co(NO ₂) ₆]	1.80	2	K ₂ bis-salicylylidene-ethylenediamine Co(II) *	2.3	6
[Co(Diarsine) ₃][ClO ₄] ₂	1.92	3	(And 17 similar substituted compounds)	2.1—2.8	6
[Co(NH ₃) ₅ NO]Cl ₂ †	1.5—1.6	4, 5	Bis-salicylaldoxime Co(II)	2.6	9
[Co(Triarsine) ₂][ClO ₄] ₂	<2.02	8	Bis- <i>o</i> -aminophenol Co(II)	2.5	9
			Bisdimethylglyoxime Co(II)	2.6	9
			Bisbenzylmethylglyoxime Co(II)	2.7	9
			Bisbenzildioxime Co(II)	2.16	9
			Bisrubeanic acid Co(II)	2.9, 2.8	9
			Bisthiosemicarbazide Co(II)	2.3	9
			Bisxanthic acid Co(II)	2.4	9
			Co(II) Phthalocyanine	2.9	10
			Co(II) Protoporphyrin dimethyl ester	2.8	11
			Bis-salicylylidenepropylenediamine Co(II)	2.48	12
			Bismonobenzylglyoxime Co(II) ...	2.21—2.14	13
			Co ethylene biguanidinium sulphate	2.6	14
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* Mellor and Craig (ref. 9) have reported a moment of 1.76 B.M. for this compound. However, Dr. Mellor (personal communication to R. S. N.) has pointed out that as no precautions to exclude oxygen were observed [shown to be essential by Calvin *et al.* (ref. 6)] this value is almost certainly too low.

† It must be emphasised that the presence of Co(II) in this compound is by no means certain.

1, Cambi, Ferrari, Coriselli, Solenghi, and Colla, *Gazzetta*, 1935, **65**, 1162. 2, Ray and Sahu, *J. Indian Chem. Soc.*, 1946, **23**, 161. 3, Burstall and Nyholm, *J.*, 1952, 3570. 4, Ray and Ghosh, *J. Indian Chem. Soc.*, 1943, **20**, 409. 5, Mellor and Craig, *J. Proc. Roy. Soc. N.S.W.*, 1944, **78**, 25. 6, Calvin, Bailes, Wilmarth, and Barkelew, *J. Amer. Chem. Soc.*, 1946, **68**, 2267. 7, Cambi, *Gazzetta*, 1935, **65**, 322. 8, Barclay and Nyholm, *Chem. and Ind.*, 1953, 378. 9, Mellor and Craig, *J. Proc. Roy. Soc. N.S.W.*, 1941, **74**, 475. 10, Senff and Klemm, *J. prakt. Chem.*, 1939, **154**, 73. 11, Falk and Nyholm, unpublished experiments. 12, Mellor and Craig, *J. Proc. Roy. Soc. N.S.W.*, 1942, **75**, 157. 13, Cambi, *Rend. Ist. Lombardi Sci.*, 1938, **71**, 85. 14, Ray and Ghosh, *J. Indian Chem. Soc.*, 1943, **20**, 323.

energy level. This triplet is split by the small rhombic field component invariably present into three levels separated by energy intervals $< kT$; each of these sub-levels is occupied to an extent dependent upon the relative size of kT and of the energy intervals. The orbital contribution is now no longer small and the moments are expected to lie somewhere between

14 Magnetic Moments and Stereochemistry of Cobaltous Compounds.

the spin only value of 3.88 B.M. and the Boltzmann value of 5.2 B.M. with a considerable orbital contribution and with high anisotropy. On the other hand, moments closer to the "spin only" value are expected for tetrahedral complexes. Experimentally it is found that tetrahedral complexes have moments in the range 4.3—4.7 B.M. with low anisotropies, whilst those of octahedral complexes are in the range 4.8—5.6 B.M. with high anisotropies (Bose, *Indian J. Phys.*, 1948, **22**, 33; Kanekar, Thesis, London, 1953). This is in general agreement with theoretical expectations.

The case when the ligands are attached to the Co(II) atom by "lower-level covalent bonds" has not been examined theoretically and the problem is one of considerable difficulty. However, an examination of all the available experimental data (Table 2) shows a good correlation between stereochemistry and orbital contribution. Both six- and four-covalent Co(II) complexes containing one unpaired electron are known; the six-covalent compounds are undoubtedly octahedrally co-ordinated, e.g., the $[\text{Co}(\text{NO}_2)_6]^{4-}$ ion (Sidgwick, "The Chemical Elements," Oxford, 1950, p. 1447), whilst the four-covalent compounds are assumed to be invariably square planar. The latter assumption is based partly on Pauling's theory relating stereochemistry and magnetism; the presence of one unpaired electron indicates the use of $3d4s4p^2$ square bond orbitals as in the corresponding diamagnetic bivalent nickel complexes (see Table 1). Experimental support for the square arrangement is provided by X-ray studies on certain quadridentate Co(II) complexes used as oxygen carriers (Calvin, Bailes, Barkelew, and Wilmarth, *J. Amer. Chem. Soc.*, 1946, **68**, 2267). The hypothesis is also supported by the fact that Co(II) complexes which are necessarily square owing to the steric requirements of the ligand, e.g., Co(II) phthalocyanine, contain one unpaired electron.

Table 2 shows that the octahedral complexes have uniformly low orbital contributions, whereas the orbital contribution in square complexes is much larger; the high magnetic moments of the (necessarily) square protoporphyrin and phthalocyanine complexes are especially noteworthy. It should be mentioned that, although the actual orbital increment over the spin only value is smaller for square covalent compounds than it is for octahedral ionic compounds, the *ratio* orbital contribution : "spin only" moment is of the same order in both cases. This suggests that an explanation based on energy level intervals $\gg kT$ and $< kT$ for the covalent octahedral and square arrangements respectively is applicable here also. However, the use of lower *d* orbitals or, what is equivalent, the presence of "strong" crystalline fields (Orgel, *J.*, 1952, 4756) precludes couching of the explanation in terms of free-ion spectroscopic states as was done in the case of so-called "ionic" bonds.

It is proposed that the size of the orbital contribution in "covalent" Co(II) complexes may be used as an empirical criterion of stereochemistry even though a detailed theoretical basis is not yet available. In short, those Co(II) complexes for which μ lies between the "spin only" value of 1.73 and 2.0 B.M. may be taken as octahedral and those for which μ lies between 2.1 and 2.9 B.M. can be regarded as square planar. The only exception to this generalisation appears to be five-covalent Co(II) complexes; only two of these have been reported—the complex cyanide $\text{K}_3\text{Co}(\text{CN})_5$ (Adamson, *J. Amer. Chem. Soc.*, 1950, **72**, 4030; 1951, **73**, 5710) and the trisertiary arsine complex $\text{CoBr}_2\text{Triarsine}$ (Barclay and Nyholm, *Chem. and Ind.*, 1953, 378). The former is diamagnetic in the solid state but has a moment *ca.* 1.7 B.M. in solution. Although it is possible that the anion is hydrated to give the octahedral $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ ion, Adamson (*loc. cit.*) considers this improbable. The absence of an energetically favourable vacant orbital to accommodate the sixth ligand without the unlikely promotion of two electrons also makes this improbable. The moment of the triarsine complex is < 2.02 B.M. The evidence supporting the conclusion that this is five- rather than four-covalent is discussed by Barclay and Nyholm (*loc. cit.*) In all but one of the octahedral complexes quoted the six groups attached to the Co(II) atom are identical and the question arises whether a small orbital contribution would still be expected in a complex of the type $[\text{CoX}_4\text{Cl}_2]^0$ wherein X is a neutral donor group. It seems most unlikely that the crystalline field would differ very much from the usual cubic symmetry of the octahedral case and in any case, on the "promotion" theory discussed below, the unpaired electron should still have a negligibly small orbital contribution.

The simple Pauling theory of "promotion" of electrons to make available orbitals for

bond formation gives some theoretical support for the empirical rule. As shown in Table I, the use of $3d^24s4p^3$ bond orbitals makes it necessary to promote the unpaired electron above the $4p$ level and it would almost certainly occupy the next orbital of lowest energy available, which is a $5s$. Such an electron is in an S state, and the moment is expected to agree fairly closely with the "spin only" value of 1.73 B.M. The small orbital contribution in octahedral complexes shows that this indeed is the case. It is of interest to note that octahedral Ni(III) complexes, which are iso-electronic with Co(II), similarly have only a small orbital contribution (Burstall and Nyholm, *loc. cit.*). On the same model, the square Co(II) complexes use $3d4s4p^2$ bond orbitals, the unpaired electron being in the $3d$ shell. Of the nine electrons now in the $3d$ shell, one pair is used for bond formation, three pairs are free, and one electron is unpaired; as a result the magnetic behaviour might be expected to be complicated. It is not possible to regard the atom as being in a D state, as with a Cu^{2+} ion, and hence interpretation in terms of the theory used when in discussions of "ionic" bonds is more difficult. However, a study of the anisotropy and temperature dependence of susceptibility for both octahedral and square covalent compounds should prove of considerable value. It may well prove that when the moments of octahedral complexes are calculated from the expression $\mu = 2.84\sqrt{\chi_M(T + \theta)}$, in which the θ correction is allowed for, they will approximate even more closely to the "spin only" value for one unpaired electron. Such studies are now being carried out in these laboratories.

It is possible that the size of the orbital contribution in covalent cobaltous complexes may prove of value in predicting the stereochemistry in compounds of biological importance, and reference has already been made to the abnormally high magnetic moments of the phthalocyanine and protoporphyrin Co(II) complexes.

The authors are indebted to Professor D. P. Craig for valuable discussions.

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[Received, July 6th, 1953.]