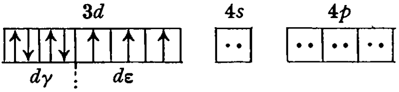
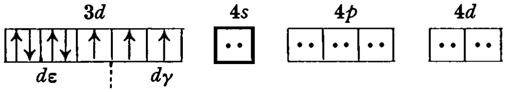
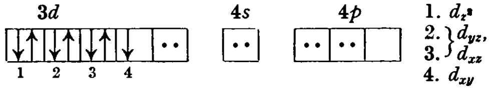
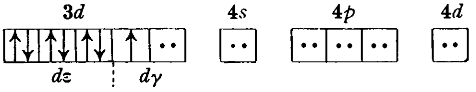
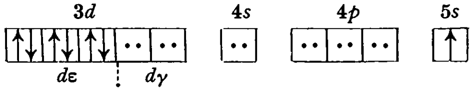
61. *Magnetochemistry. Part II.* The Temperature-dependence of the Magnetic Susceptibility of Bivalent Cobalt Compounds.*

By B. N. FIGGIS and R. S. NYHOLM.

The magnetic susceptibilities of a number of quadri- and sexa-covalent cobalt(II) complexes from 80° to 300° K are reported. The size of the orbital contribution to the magnetic moment is determined and is correlated with the co-ordination number and stereochemistry. Values of the Weiss constant (θ) are small and the moments in the range 1·9—2·0 B.M. and 2·1—2·9 B.M. for the octahedral and square spin-paired complexes respectively are sensibly the same over the temperature range studied. The significance of the moments of spin-free octahedral and tetrahedral complexes is also discussed.

THE correlations between stereochemistry and orbital contribution to the magnetic moment in compounds of bivalent cobalt[1] are summarised in Table 1. The existence of a relatively large orbital contribution to the moment in octahedrally co-ordinated compounds of the spin-free (or so-called " ionic ") type, and of a smaller contribution in tetrahedrally co-ordinated compounds of the same type, is paralled in a modified form by the behaviour of compounds of the spin-paired (or so-called " covalent " type). In the latter type, however, it was found that, although sexacovalent complexes were characterised by the virtual absence of orbital contribution, yet in the square co-ordinated compounds this may have an appreciable value. To our previous list,[1] on which we based the association of stereochemistry with orbital contribution for the spin-paired compounds, may be added

TABLE 1. *Electronic configurations of various cobaltous complexes.*

Type of complex	Co-ordination no. and stereochemistry	Electronic configuration	Unpaired electrons
Spin-free	Quadricovalent tetrahedral		3
	Sexacovalent octahedral		3
Spin-paired	Quadricovalent square planar †		1
	Sexacovalent (presumably tetragonal) (a)		1
	(b) *		1

The symbol $\boxed{\cdot\cdot}$ indicates the bonding orbitals (if used).
* Originally proposed [1] but now considered improbable.
† From Fig. 1; see also ref. 22.

---

* Part I, preceding paper.

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

the following measurements which support the previous proposals. The moment of the complex of bivalent cobalt with the sexadentate ligand

$$HO{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}[CH_2]_2{\cdot}S{\cdot}[CH_2]_2{\cdot}S{\cdot}[CH_2]_2{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH$$

is 1·82 B.M.[2] Two compounds of the quadricovalent type, [Co(*o*-aminobenzenethiol)$_2$]^0, *i.e.*, $[Co(NH_2{\cdot}C_6H_4{\cdot}S)_2]^0$, and [Co(ethylthiopropanethiol)$_2$]^0, *i.e.*, $[Co(CH_3{\cdot}CH_2{\cdot}S{\cdot}[CH_2]_3{\cdot}S)_2]^0$, have been reported to have moments of 2·7 and 2·5 B.M. respectively.[3]

Most previous magnetic measurements on cobalt(II) complexes were for one temperature only and the interpretation of values of μ_{eff} calculated them was uncertain. Our measurements were undertaken to obtain results as to the separation between possible energy levels (relative to kT) and information concerning the ground states of the various types of cobaltous compound. In particular it was desired to establish (i) that the large orbital contribution occurring in the octahedral *weak field* and the square-planar *strong field* cases are " genuine " in so far as they are maintained over a range of temperature; (ii) to find whether the simple ground states suggested by the close to spin-only value moments are confirmed by simple magnetic behaviour with regard to temperature.

The orbital contribution of spin-free cobaltous compounds arises as follows. The ground term of the Co^{2+} ion, d^7, is ^4F; there are three unpaired electrons and the ion is seven-fold degenerate with respect to electric fields. An octahedral arrangement of ligand atoms about the central cobalt ion gives rise to a crystalline field of cubic symmetry which splits the seven levels of the F state into two orbital triplet sets and a singlet one, with separations between those of the order of 20,000 cm.$^{-1}$. One of the triplets, predominantly $d_\epsilon^5 d_\gamma^2$, lies lowest. The orbital angular momentum of the ion results from orbital degeneracy, or near degeneracy if fields of less than cubic symmetry are present, within this triplet.[4] For this d^7 three-spin system the magnetic moments should lie somewhere between the limits $\mu_{eff} = \sqrt{[4S(S+1)]} = 3{\cdot}88$ B.M. and $\mu_{eff} = \sqrt{[4S(S+1) + L(L+1)]} = 5{\cdot}2$ B.M., where S is the total spin angular momentum of $(3/2)h/2\pi$ and L is the total orbital angular momentum of $3h/2\pi$. The actual value depends upon the amount of L remaining associated with the ground-state orbital triplet. On the other hand, when the ligand arrangement about the cobalt atom is tetrahedral there is again a cubic field set up, but it is now of opposite sign to that of the octahedral case so that in these circumstances the ground orbital state is the singlet. As there is no orbital angular moment associated with the singlet level the moment for the system is expected to lie close to the spin-only value.

In fact some orbital contribution occurs in the tetrahedral complexes, for experimental moments mostly lie in the range 3·9—4·4 B.M. This orbital contribution is considered to arise from the mixing of some of the next higher orbital triplet level into the singlet by the operation of spin-orbit coupling; the spin-only moment is multiplied by a factor $(1 + 4A/3\Delta)$. The value of Δ is probably about 5000 cm.$^{-1}$ for tetrahedral complexes and A is the *single* electron spin-orbit coupling constant, 540 cm.$^{-1}$. Then μ_{eff} is expected to be ~4·5 B.M. The theory of the spin-paired case is not well developed. The unpaired electron of the spin-paired hexaco-ordinated cobalt(II) compounds may be accommodated either in the d_γ orbitals or, less likely, " promoted " to a $5s$ orbital. Although we originally favoured the latter we now consider this improbable (see Table 1). In either case, however, the magnetic properties of the system should be simple and devoid of orbital contribution since neither a $3d_z{}^2$ nor a $5s$ electron should give rise to orbital magnetism.

The effect of a strong tetragonal field on the magnetic properties of the d orbitals has not been considered in detail: it seems that the splittings will be as shown in Fig. 1. In a strong tetragonal field the concept of d_ϵ and d_γ orbitals loses much of its significance. If the field arises from four ligand atoms, regarded as point charges, placed at a distance a

---

[2] Dwyer, Gill, Gyarfas, and Lyons, *J. Amer. Chem. Soc.*, 1957, **79**, 1269.

[3] Livingstone, *J.*, 1957, 143.

[4] Abragam and Pryce, *Proc. Roy. Soc.*, 1951, *A*, **206**, 173.

from the central metal atom and on the x and y axes of the Cartesian system, the positions of the energies of the orbitals, relative to the centre of gravity, are:

$$d_{z^2} \text{ at } -\left(\frac{6}{a^3}\overline{r^2} - \frac{9}{2a^5}\overline{r^4}\right)\frac{2Z}{105}\,; \qquad d_{xz} \text{ and } d_{yz} \text{ at } -\left(\frac{3}{a^3}\overline{r^2} + \frac{3}{a^5}\overline{r^4}\right)\frac{2Z}{105}$$

$$d_{xy} \text{ at } \left(\frac{6}{a^3}\overline{r^2} - \frac{8}{a^5}\overline{r^4}\right)\frac{2Z}{105}\,; \qquad d_{x^2-y^2} \text{ at } \left(\frac{6}{a^3}\overline{r^2} + \frac{19}{2a^5}\overline{r^4}\right)\frac{2Z}{105}$$

where Z is the charge assumed on the ligand atom and r is the radius from the central ion. We may compare these splittings with the d_ϵ–d_γ separation for the octahedral case which differs from the tetragonal case by the placing of two additional charges in the octahedral positions:[5]

$$d_\epsilon \text{ at } -\frac{4}{a^5}\overline{r^4}\cdot\frac{2Z}{21}\,; \qquad d_\gamma \text{ at } \frac{6}{a^5}\overline{r^4}\cdot\frac{2Z}{21}$$

In Fig. 1 are the separations for the square planar arrangement and for a metal ion–ligand atom separation of about 3 Å. An exact comparison of the separations with the d_ϵ–d_γ separation would require a knowledge of the values of $\overline{r^2}$ and $\overline{r^4}$ for the Co^{2+} ion but, in view of the crudeness of the picture upon which the calculations are based, it is likely that a quantitative comparison would be of little value. It seems probable, if reasonable values of $\overline{r^2}$ and $\overline{r^4}$ are assumed (*e.g.*, $3a_0^2$ and $30a_0^4$, respectively; a_0 is the atomic unit of length), that the energy separation $d_{xy} - d_{x^2-y^2}$ in the square planar case is of the order of the $d_\epsilon - d_\gamma$ separation in the octahedral case.

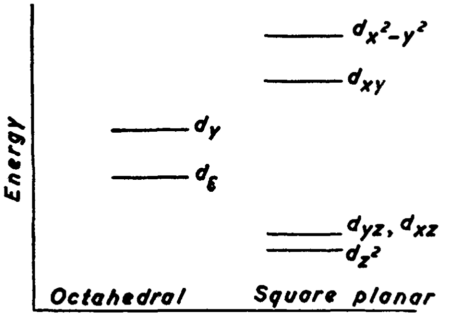


FIG. 1. *The splittings of the d orbitals in the field of four charges in a plane* ($\pm a$, 0, 0), (0, $\pm a$, 0); a = 3 Å, $\overline{r^2} = 3a_0^2$, $\overline{r^4} = 30a_0^4$.
The d_ϵ and d_γ levels are given for the same conditions with charges in octahedral positions.

If the order of the levels for the square planar case is as in Fig. 1 with separations between the levels corresponding to a strong field, *i.e.*, sufficient to force spin pairing, then the seven electrons of cobalt(II) would be distributed as follows: 2 in the d_{z^2} orbital, 4 in the d_{xz} and d_{yz} orbital set, and finally one in the d_{xy} orbital, and it is the last one alone which is responsible for the magnetic properties of the system. The moment should correspond to the spin-only value for one unpaired spin multiplied by a factor $\sim (1 + 2A/\Delta)$, Δ being the separation between the d_{xy} orbital and its neighbouring levels. However, this effect is sufficient to account for moments of only about 10% above the spin-only value, *i.e.*, up to about 2·0 B.M.

Dependence of the Susceptibility on Temperature.—The theory of the magnetic behaviour of the triplet ground level from the ^4F term of Co^{2+} has been developed in detail by Penney and Schlapp,[6] particularly for the Tutton salts, *e.g.*, $(NH_4)_2Co(SO_4)_2,6H_2O$, assuming that fields of predominantly cubic symmetry but with rhombic components were operative. However, as those authors did not have adequate data on the crystal structures, agreement between experiment and the theory, while encouraging, was not close. Owing to

---

[5] Bethe, *Ann. Physik*, 1929, **3**, 133.
[6] Penney and Schlapp, *Phys. Rev.*, 1932, **41**, 242, 666.

the fact that the ground level considered was the orbital triplet the treatment was difficult. They were able to account approximately for the room-temperature moment of 5·2 B.M., its decrease to 4·4 B.M. at 80° K, and the magnetic anistropy. The theory of the magnetic properties of the tetrahedrally co-ordinated type of cobaltous compound has not been given in such detail although Bose [7] dealt with it to some extent. It appears that the singlet ground state which is involved should be subject to no obvious effects which disturb the expected simple magnetic behaviour; there seems to be no reason for expecting departures from Curie's law. However, in view of the small orbital contributions which do occur some interest arises as to whether these are accompanied by deviations from Curie's law.

As far as the spin-paired or strong-field case is concerned no theoretical treatment of the temperature-dependence of the susceptibility has been attempted; the most that can be said is that the approximation of the octahedral type of compounds to the spin-only value of the moment at room temperature is very likely to be an indication of magnetic simplicity which should be paralleled by conformity with a Curie law. On the other hand, the lack of magnetic simplicity shown by the very appreciable orbital contribution in the square-planar compounds is likely to be reflected in a somewhat more complicated magnetic behaviour with temperature.

Published experimental data on the temperature-dependence of the magnetic susceptibility of cobaltous compounds are not extensive and are confined almost entirely to the spin-free or weak-field case. The Tutton salts $(NH_4, K, Rb)_2Co(SO_4)_2,6H_2O$ as well as $CoSO_4,7H_2O$ were studied in terms of the magnetic anisotropy by Jackson,[8] but at only three temperatures between 15° and 300° K, and doubt has been cast on the reliability of these results.[9] The same Tutton salts, together with Cs_2CoCl_4 and $CoBeF_4,7H_2O$, were studied by Bose,[7] and Guha [10] deal with $CoSO_4,7H_2O$ and $CoSeO_4,7H_2O$. These measurements also were primarily concerned with the anisotropy of the magnetic susceptibility. Amonst the spin-paired compounds Calvin and others [11] studied the susceptibility of the square compounds Co(ethylenediaminebis-salicylaldehyde) in both "active" and "inactive" forms and also the 3-methoxy- and the pyridine derivative of this compound. The rather extraordinary magnetic behaviour of the first two of these compounds, combined with the difficulty of being sure of their actual chemical identity, renders the significance of the measurements doubtful. The last of these compounds may have involved a quinquecovalent stereochemistry for the cobalt atom.

The values of θ reported in connection with the above measurements on the spin-free octahedral compounds vary from 15° to 30°; such values are as might have been expected for such a system. The only available result for the tetrahedral arrangement is 7° for θ for the compound Cs_2CoCl_4; this is distinctly lower than those for the octahedral case but not the vanishingly small value that a perfectly simple ground state requires: it is rather in line with the small amount of orbital contribution exhibited. For the spin-paired type of compound data are available only for the square-planar case, where θ values from −20° to 60° are reported; but little of significance can be deduced from this since the nature of the compounds concerned and the precision of the magnetic measurements are not well established.

Discussion.—The compounds studied are listed in Table 2.

(a) *Octahedral spin-free.* In common with all the Tutton salts, $(NH_4)_2Co(SO_4)_2,6H_2O$ crystallises with an octahedron of water molecules, slightly distorted by elongation in one axis, about the central cobalt atom.[12,13] The distortion of the octahedron must result in

---

[7] Bose, Thesis, Dacca University, 1946.

[8] Jackson, *Phil. Trans.*, 1923, **224**, 1.

[9] Banjeri, Chakrovooty, and Krishnan, *Phil. Trans.*, 1933, **232**, 99.

[10] Guha, *Proc. Roy. Soc.*, 1951, *A*, **206**, 353.

[11] Barkelew and Calvin, *J. Amer. Chem. Soc.*, 1946, **68**, 2257.

[12] Hoffmann, *Z. Krist.*, 1930, **75**, 158; 1931, **78**, 279.

[13] Halla and Mehl, *Z. anorg. Chem.*, 1931, **199**, 379.

TABLE 2. *Diamagnetic corrections, magnetic moments at* 300° *and* 90° K, θ *values, and accuracies of the measurements of the relative susceptibilities at different temperatures for the compounds of bivalent cobalt studied.*

Stereochemistry and type		Diam. Corr. × 10^6	μ_{eff} 90° K	μ_{eff} 300° K	θ (°)	Accuracy (%)
Octahedral, 3 unpaired electrons	$(NH_4)_2Co(SO_4)_2,6H_2O$	184	4·53	4·90	27	0·5
	$Co(o\text{-phen})_3(ClO_4)_2$ [a]	394	5·54	4·70	11	0·5
	$KCo(\text{acetylacetone})_3$	192	5·02	4·70	−15	2
Tetrahedral, 3 unpaired electrons	$HgCo(CNS)_4$	137	4·18	4·33	10	0·5
	$Co(Ph{\cdot}NH_2)_2Cl_2$	167	3·96	4·19	27	1
Octahedral, 1 unpaired electron	$K_2BaCo(NO_2)_6$	147	1·73	1·88	25	1
	$K_2PbCo(NO_2)_6$	150	1·74	1·81	5	1
Square-planar, 1 unpaired electron	$CoD_2(ClO_4)_2$ [b]	454	1·98	2·10	10	0·5
	Co(phthalocyanine)	290	2·22	2·72	(60) [c]	1
	Co(en.sal.) [d]	151	2·06	2·24	25	1
	Co(E.T.T.) [e]	184	2·38	2·54	17	0·5

[a] *o*-Phen = *o*-phenanthroline. [b] D = *o*-Phenylenebisdimethylarsine. [c] It is not really justified to evaluate a θ in this case. [d] en.sal. = ethylenedi-iminebis-salicylaldehyde. [e] E.T.T. = ethylthiopropanethiol.

a tetragonal field of some magnitude, but this does not affect the essential arguments concerning the contribution of an orbital term to the moment by the triplet-type ground state. There is *X*-ray [14] evidence that the cobalt atom in $[Co(o\text{-phenanthroline})_3](ClO_4)_2$ is octahedrally co-ordinated. Although one would confidently expect an octahedral stereochemistry for the cobalt in $K[Co(\text{acetylacetone})_3]$, some slight deviations from perfect symmetry in the crystal are probable because the ground state is only approximately $d_\epsilon{}^5 d_\gamma{}^2$, the ions outside the co-ordination sphere influence packing of the lattice, and the ligand is bidentate. Table 2 shows that the values of θ for these compounds of the octahedral weak-field type are 27°, 11°, and −15°. The 27° for $(NH_4)_2Co(SO_4)_2,6H_2O$ agrees quite well with the value of 22° reported by Jackson, considering that his value was obtained by averaging the results of anisotropy measurements. Such values of θ are of the same order as those in the literature; they show that, although the system is not magnetically simple, the deviations are not sufficiently large seriously to affect the moments concerned at any temperature studied. The orbital contribution involved is maintained substantially unchanged by temperature variation over the range of measurement.

(b) *Tetrahedral spin-free.* $HgCo(CNS)_4$ is known from *X*-ray evidence [15] to be formed by the sulphur atoms of each (CNS) group surrounding the cobalt atom tetrahedrally, the nitrogen atoms of that group being attached to four different mercury atoms which are also thus tetrahedrally co-ordinated. For this tetrahedral weak-field case the situation is not quite as much in conformity with expectations: in addition to Bose's value of 7° for Cs_2CoCl_4, we find values of 10° and 27° for θ pertaining to the compounds of the group. Values of θ as large as this are not to be associated with a ground state as simple as described above. Of course, θ values of this magnitude do not significantly affect the moments involved over the temperature range concerned, and the orbital contribution to the moment is clearly quite small. However, the lack of magnetic simplicity indicated is sufficient to warn us against taking too seriously the resemblance between the orbitally single ground state arising from the splitting of an *F* state and an *S* state.

(c) *Sexacovalent spin-paired.* A regular octahedral co-ordination of nitrite groups around the central cobalt atom in the cobaltonitrites has been reported by Ferrari and others [16] from *X*-ray studies. This is rather unexpected since, if the single unpaired *d* electron is in a d_γ (presumably d_{z^2}) orbital, a *lengthening* along one axis (*z*) of the octahedron is expected. It is unfortunate that other compounds of the octahedral strong

---

[14] Harris and Stevenson, unpublished work.

[15] Jeffery, *Nature*, 1947, **159**, 1620.

[16] Ferrari and Colla, *Atti Accad. Lincei*, 1930, **11**, 755; 1932, **14**, 435.

field case of cobalt(II) were not available in addition to the cobaltonitrites, but none of sufficiently substantiated constitution could be obtained. The value of θ for the two cobaltonitrites studied show a disagreement rather surprisingly large in view of the high degree of similarity that one expects between the environments of the cobalt atoms in the compounds. Once again, although the magnetic complexity is not sufficiently great to affect the conclusion that orbital contribution is negligible for the system, it is obvious that the ground state is not entirely simple. The assumption that the unpaired electron is accommodated in a pure d_{z^2} orbital must not be taken literally.

(d) *Quadricovalent spin-paired.* Apart from the phthalocyanine derivative, known from *X*-ray evidence to be square planar, in common with all the other phthalocyanines,[15] structural information is lacking for the compounds of the tetraco-ordinated spin-paired type; the assignment of a square stereochemistry is made principally on magnetic evidence. For the compound [Co(ethylenedi-iminebis-salicylaldehyde)]^0, for which the values of θ of 60° and 0° (according as the form was " active " or " inactive " as an oxygen carrier) have been reported; [11] we find the value of 25°. The values of θ found for the other compounds of the square type were 10, 17, and, perhaps, 60°. The value of 60° is that assigned to the phthalocyanine derivative but the significance of the quantity in connection with this compound is a matter of conjecture, for the magnetic behaviour is quite anomalous. The variation of the susceptibility with temperature may be described by means of an expression of the form of a Curie–Weiss law in combination with a large term for the susceptibility independent of temperature, but probably not much physical significance can be attached to the individual terms of the expression; the moment at 80° K agrees with that calculated from the paramagnetic resonance *g* values taken at 14° K.[17] The remaining θ values again are of an order of magnitude which indicates some appreciable lack of magnetic simplicity in the ground state of the system but do not much affect the moment. The orbital contribution to the moment in these compounds is obviously not very dependent on temperature. The origin of the large orbital contribution in the square-planar type compounds is still not understood. The simple application of ligand-field theory discussed earlier does not satisfactorily account for moments of more than about 2·0 B.M. The theory neglects the possibility of the octahedral positions' being effectively filled, at least to some extent, by atoms other than ligands directly bonded to the metal atom in the solid state. This effect could drastically affect the assignment of levels given in Fig. 1, particularly in raising the energy of the d_{z^2} orbital in relation to the others. The effects produced by π bonding could also be of more importance in determining the distribution of the magnetic electrons than in the octahedral case. These considerations have recently been discussed in detail in reference to some phthalocyanines.[17]

The conclusion reached from the study of the available information on the temperature-dependence of the susceptibility of bivalent cobalt compounds is that the association of the presence of an orbital contribution to the moment with certain conditions of stereochemistry and bond type is confirmed. However, there does not seem to be the difference in the magnetic complexity of the ground states of the systems that do and do not give rise to this orbital contribution that the theory of the effect suggests.

The small curvature in the susceptibility–temperature curves for the one unpaired-electron type compounds at higher temperatures is due to the presence of a small term independent of temperature, of the order of 60×10^{-6} i.g.s.u./mole, in the susceptibility. This effect will be discussed in detail in a later Part. It was not appreciable in the three unpaired electron case, as the Curie law susceptibilities then are so much larger.

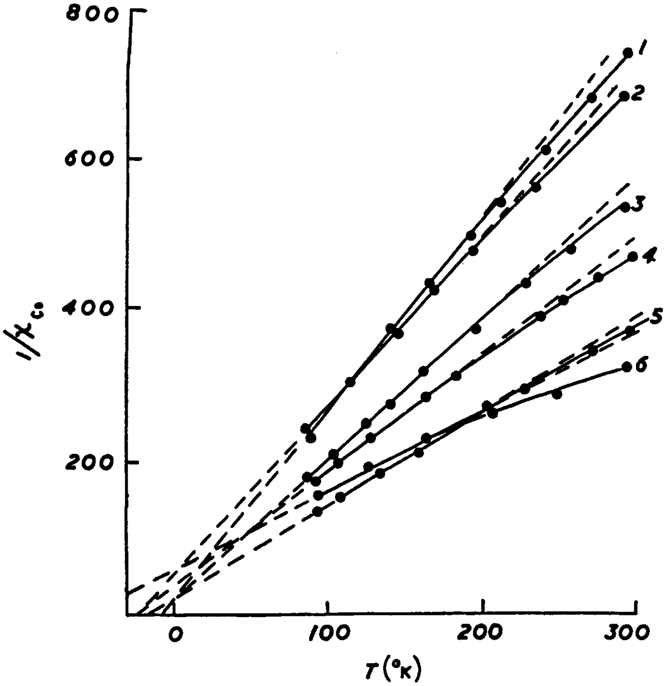
EXPERIMENTAL

The temperature-dependence of the magnetic susceptibility was measured as described in Part I (preceding paper). The inverse of the corrected molar susceptibility is plotted against the temperature in Figs. 2 and 3. In Table 2 the corrections for diamagnetism, the moments

---

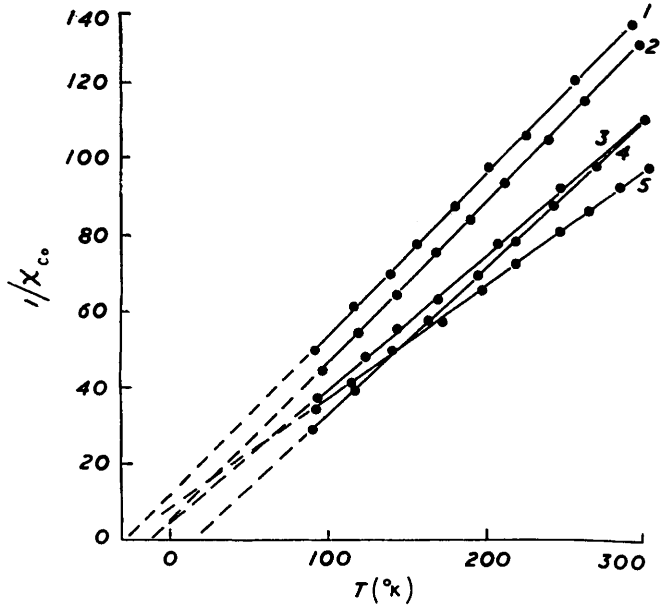
[17] Griffith, Gibson, Ingram, and Scholand, *Discuss. Faraday Soc.*, Dublin, September, 1958.

FIG. 2. *Inverse of corrected molar susceptibility* versus *temperature.*



1, $K_2PbCo(NO_2)_6$; 2, $K_2BaCo(NO_2)_6$; 3, Co(*o*-phenylenebisdimethylarsine)$_2$(ClO_4)$_2$; 4, Co(ethylene-di-iminebis-salicylaldehyde); 5, Co(ethylthiopropanethiol); 6, Co(phthalocyanine).

FIG. 3. *Inverse of corrected molar susceptibility* versus *temperature.*



1, Co($Ph{\cdot}NH_2$)$_2$$Cl_2$; 2, HgCo(CNS)$_4$; 3, KCo(acetylacetone)$_3$; 4, Co(*o*-phenanthroline)$_3$(ClO_4)$_2$; 5, $(NH_4)_2Co(SO_4)_2,6H_2O$.

at the extremes of the temperature range, values of θ, and the accuracy of the measurement of the relative susceptibility at different temperatures are given. Corrections for the diamagnetic portions of the molecule were obtained either from Pascal's constants or by direct measurement of the diamagnetic portion of the molecule. No correction was included for the diamagnetism of the paired electrons of the filled shells of the cobalt atom itself. Values of θ were obtained by extrapolating the lower-temperature part of the inverse susceptibility–temperature curve to infinite susceptibility; the intercept on the temperature axis then gave the negative of θ.

"AnalaR" $(NH_4)_2Co(SO_4)_2,6H_2O$ was used. Specimens of $[Co(o\text{-phenanthroline})_3][ClO_4]_2$ and $[Co(o\text{-phenylenebisdimethylarsine})_2][ClO_4]_2$ were kindly supplied by Dr. C. Harris (University of New South Wales, Sydney). The specimens of $[Co(phthalocyanine)]^0$, purified by repeated high-vacuum sublimation, and $[Co(ethylthiopropanethiol)]^0$ were kindly supplied by Mr. P. Fielding and Dr. S. Livingstone respectively of that University. The specimen of $K[Co(acetylacetone)_3]$ was lent by Mr. A. Sargeson (University of Sydney). The cobaltonitrites were prepared as described in the literature,[18, 19] with care during the preparation and subsequent handling to prevent oxidation. $[Co(Ph{\cdot}NH_2)_2Cl_2]^0$ and $HgCo(CNS)_4$ were prepared by mixing together the constituents in alcoholic and aqueous solutions respectively. $[Co(ethylenediaminebis\text{-}salicylaldehyde)]^0$ was prepared by adding equimolar proportions of cobaltous chloride and the ligand in alcohol; the preparation, handling, and measurement of the susceptibility were conducted in an atmosphere of nitrogen to prevent oxidation of the sample.[20] These precautions were not necessary with the other compounds of the square type, which were chosen in order to avoid the effect.

INORGANIC CHEMISTRY DEPARTMENT, N.S.W. UNIVERSITY OF TECHNOLOGY,
SYDNEY, AUSTRALIA (*now* UNIVERSITY OF NEW SOUTH WALES).
WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1 [*Present address*].

[*Received, January* 6*th*, 1958.]

---

[18] Cuttica and Garobbi, *Gazzetta*, 1922, **52**, 270; Cuttica and Paoletti, *ibid.*, p. 279; Cuttica, *ibid.*, 1923, **53**, 185.

[19] Ray and Sahu, *J. Indian Chem. Soc.*, 1946, **23**, 161.

[20] Bailes, Calvin, and Wilmarth, *J. Amer. Chem. Soc.*, 1946, **68**, 2253