45. The Constitution of the Nitrosopentammine Cobalt Salts.

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Some years ago an account was published of the preparation and properties of the so-called nitrosopentammine cobalt salts. Two series of salts were described, one being red and the other black. Both series were obtained by the action of nitric oxide on ammoniacal solutions of cobaltous salts and they have the same general formula [NO, Co, $5NH_3$]X_2. Various structures have been proposed to explain the striking differences in colour and chemical properties which these salts exhibit. The present authors bring forward chemical and physical evidence which they consider proves that the red compounds are true nitroso-derivatives [NO—Co,$5NH_3$]X_2 in which the 6-covalent cobalt is tervalent; the black compounds, on the other hand, although containing 6-covalent cobalt, have a structure in which the NO group resonates and leads to the formulæ [$5NH_3$,$\overset{=}{Co}$—$\overset{+}{N}$≡$\overset{+}{O}$]X_2 and [$5NH_3$,$\overset{-}{Co}$≡$\overset{+}{N}$≡$\overset{+}{O}$]X_2 whereby the principal valency of the cobalt changes from one to three.

THE nature of the linkage formed between nitric oxide and a metallic atom has been much discussed. The obvious analogy between nitric oxide and carbon monoxide in the metallic nitrosyl and carbonyl compounds has led to the suggestion that they must be similarly constituted, but as nitric oxide has one more electron than carbon monoxide the assumption is generally made that this electron is contributed to the metal with which the NO is associated. Hieber and Anderson (*Z. anorg. Chem.*, 1932, **208**, 238; 1933, **211**, 132) consider that in the nitrosocarbonyls, such as $Co(CO)_3NO$, the NO group, having donated an electron to the metal, is then linked by a double electron-pair bond to the same metal, and that there is a double bond between the nitrogen and the oxygen atom, thus $\overset{-}{M}::\overset{+}{N}::\overset{..}{O}:$ or $\overset{+}{M}$=$\overset{}{N}$=O. On the other hand, Sidgwick and Bailey (*Proc. Roy. Soc.*, 1934, *A*, **144**, 521) maintain that this idea leads to values for the principal valency and covalency of metal atoms which cannot be entertained. They suggest that the linking is $\overset{-}{M}:\overset{+}{N}:::\overset{}{O}:$ or $\overset{=}{M}$—$\overset{+}{N}$≡O. In a recent investigation on the molecular structures of the nitrosocarbonyls of cobalt and iron by electron diffraction, Brockway and Anderson (*Trans. Faraday Soc.*, 1937, **33**, 1233) calculate that the metal–nitrogen distances are about 0·16 A. less than the corresponding single-bond distance, whilst the bond lengths in the nitroso- and carbonyl groups are intermediate between those of double and triple bonds. They conclude, therefore, that the structure of these compounds is in accordance with the resonating electronic structures (1) $\overset{=}{M}$—$\overset{+}{N}$≡$\overset{+}{O}$ and (2) $\overset{-}{M}$≡$\overset{+}{N}$=O. This idea of a resonating electronic structure for the NO group appears to explain the constitution of that curious group of compounds, the black nitroso-pentammine cobalt salts. It has been known for many years (Sand and Geissler, *Ber.*, 1903, **36**, 2083; *Annalen*, 1903, **329**, 194) that by the action of nitric oxide on an ammoniacal solution of a cobaltous salt it is possible to isolate derivatives with the empirical formula [$5NH_3CoNO$]X_2 and that these derivatives may exist in black or red modifications. It has been found that when a cobaltous halide is used, the black series results, whereas if cobaltous nitrate is employed the red modification is generally obtained. The exact constitution of the black series had not been considered in detail until 1934 when Sidgwick and Bailey suggested (*loc. cit.*) that these salts were really true nitroso-derivatives [$5NH_3Co$—NO]Cl_2, where the cobalt atom is tervalent and 6-covalent as in [$5NH_3CoCl$]Cl_2. It is difficult, however, to reconcile this structure with the properties of the black salts. In the first place we have confirmed the fact (Werner and Karrer, *Helv. Chim. Acta*, 1918, **1**, 54) that the nitric oxide is very readily liberated as such when dilute hydrochloric acid or even water is added to the black chloride, and that, as a result of the decomposition with dilute acid, the cobalt is obtained in the form of cobaltous chloride. If the black chloride were actually the cobaltic salt [$5NH_3Co$—NO]Cl_2, decomposition with hydrochloric acid should yield the very stable purpureo-chloride [$5NH_3CoCl$]Cl_2, with liberation of (NOH)$_x$ possibly as hyponitrous acid or as water and nitrous oxide. Additional

evidence against the constitution suggested by Sidgwick and Bailey is the important fact that the black chloride is paramagnetic. Ray and Bhar (*J. Indian Chem. Soc.*, 1928, **5**, 497) carried out some preliminary magnetic measurements at 29° on this black chloride which indicated paramagnetism, and we have now shown that this is actually so by measurements over the temperature range — 195° to 85°. This seems to indicate quite clearly that the black chloride is not an ammine of tervalent cobalt, for all cobaltic complexes of the series $K_3[CoCl_6]$ to $[Co6NH_3]Cl_3$ are diamagnetic. A consideration of these experimental facts makes it most probable that in the black series of compounds the NO is attached to the metal atom by the same linkages as the NO group in the nitrosocarbonyls of the metals. This would mean that the structure contains a resonating NO group, which would lead to the formulæ $[5NH_3\overset{=}{C}o\overset{+}{N}\overset{+}{\equiv}O]Cl_2$ and $[5NH_3\overset{-}{C}o\overset{+}{=}N\overset{+}{\equiv}O]Cl_2$. If the NO resonates between the structures proposed, then the principal valency of the cobalt would change from 1 to 3. The black colour of the chloride is quite in accordance with this idea, for it is generally accepted that substances showing an intermediate valency have a dark colour as in the familiar cases of the black thallo-thallic salts and the black cupro-cupric derivatives. The red salts, however, do appear to be true nitroso-compounds, as Sidgwick and Bailey suggest, but there seems no reason why they should be considered dimeric. Sand and Geissler (*loc. cit.*), who first prepared these compounds, formulated them as $(N_2O_2)[Co(NH_3)_5X_2]_2$ because the nitrate had half a molecule of water of crystallisation. It is now realised that this conclusion is unsound, for the water content will be determined by the crystal lattice. Moreover, Werner and Karrer (*loc. cit.*) could not isolate hyponitrous acid from these salts or detect it in solution. They also attempted to prepare the red salts by the action of silver hyponitrite on $[5NH_3CoCl]X_2$ but without success, and we now find, in accordance with their results, that the substance obtained from this reaction is an aquopentammino-cobaltic salt. The idea that these red salts are true nitroso-derivatives agrees well with the experimental fact that by treatment with hydrochloric acid no nitric oxide is liberated, and that the purpureo-chloride $[5NH_3CoCl]Cl_2$ separates from the solution. Even more significant is the fact that the nitrate $[5NH_3CoNO](NO_3)_2$ is diamagnetic and in this respect takes its place as a typical member of the series of ammines of tervalent cobalt.

EXPERIMENTAL.

Black Nitrosopentamminocobalt Chloride.—A hot solution of cobaltous chloride hexahydrate (25 g.; 50 c.c.) was added to ammonia (*d* 0·88; 125 c.c.) and then filtered into a nitrogen-filled flask. Nitric oxide was passed into this ammoniacal solution for about 3 hours, after which the reaction products were filtered off, and the black residue washed with ammonia (*d* 0·88), alcohol, and then ether, and dried over calcium chloride. This black crystalline powder could be kept for long periods, in the absence of moisture, without change in composition (Found : Co, 24·1; Cl, 28·8. Calc. for $[5NH_3CoNO]Cl_2$: Co, 24·0; Cl, 28·9%). The compound is insoluble in all organic solvents and is decomposed by water with liberation of nitric oxide. Addition of hydrochloric acid to the solid liberates nitric oxide and gives a blue solution characteristic of cobaltous salts.

Red Nitrosopentamminocobalt Nitrate.—A hot solution of hydrated cobalt nitrate (17 g.; 25 c.c.) was added to ammonia (*d* 0·88; 85 c.c.) and treated for several hours with nitric oxide as above. The solid product was filtered off and recrystallised from very dilute ammonia solution. After drying over calcium chloride the crystals still retained ½ H_2O (Found : Co, 19·2; NH_3, 27·8. Calc. for $[5NH_3CoNO](NO_3)_2,0·5H_2O$: Co, 19·2; NH_3, 27·6%). This compound is insoluble in the ordinary organic solvents but soluble and stable in water. With cold concentrated hydrochloric acid it yields $[5NH_3CoCl]Cl_2$ (Found : Co, 23·6. Calc. : Co, 23·56%).

Magnetic Susceptibility of Nitrosopentamminocobalt Chloride and Nitrate.—*Chloride.* Measurements on the magnetic susceptibility of the two foregoing salts have been made for the temperature interval — 195° to 85° by means of the Gouy method, in which a glass tube containing the substance under investigation is suspended with its axis at right angles to a homogeneous magnetic field, one end of the tube being in the field and the other end in a region where the field is negligible. The force (in dynes) acting on the substance is $f = \frac{1}{2}(\kappa - \kappa_m)sH^2$, where κ and κ_m are the volume susceptibilities respectively of the substance and of the surrounding medium, H is the value of the magnetic field, and s the inside cross-section of the tube. The

force f, is determined by means of a balance sensitive to 0·02 mg. The tube is suspended in a slightly larger tube, which is itself surrounded by a Dewar flask where various baths maintain a constant temperature. Level with each end of the sample holder severally are two copper–constantan thermocouples. The glass tubes used for holding the substances were 10 cm. long; they were of special Jena glass with a precise inside diameter correct within 0·01 mm. They had an inside cross diameter of 3 or 4 mm. A correction is made for the magnetism of the tube itself.

The measurements were made at the temperature of liquid air and solid carbon dioxide and also for a range between 0° and 90°. The calibration of the apparatus was made with solid manganese sulphate, whose mass susceptibility is taken to be $\chi_s = + 83\cdot1 \times 10^{-6}$ at 16°, and also with cerous chloride hexahydrate, whose mass susceptibility is $6\cdot06 \times 10^{-6}$ at 18°.

Measurements at room temperature (17°). In the following tables, f is the force (in mg.) acting on the tube containing a column of length l cm. of the substance under investigation, f_s, the force acting on the paramagnetic salt used as standard (manganese sulphate or cerous chloride) for the same length l, f_t is the force exerted on the empty tube, p and p_s the weights (in g.) respectively of the ammine and of the standard substance, χ_1 the gram susceptibility of nitrosopentamminocobalt chloride, and χ_s that of the standard. κ_{mi} being negligible compared with κ, χ_1 is given by the formula $\chi_1 = f p_s \chi_s / f_s p$.

The data given below are believed to be accurate to 2—2·5%. The values obtained for χ_1 are

Diam. of tube, mm.	l.	l_s.	f_t.	f.	p.	MnSO$_4$.		CeCl$_3$,6H$_2$O.		$\chi_1 \times 10^6$.
						f_s.	p_s.	f_s.	p_s.	
4	8·244	8·222	−0·78	3·96	0·81562	124·30	1·1909	—	—	3·86
4	8·278	8·270	−0·78	3·94	0·82126	120·41	1·1772	—	—	3·89
4	—	8·220	−0·78	3·94	0·82126	—	—	12·94	1·73142	3·88

converted into molecular susceptibilities, χ_m, by multiplying by the molecular weight 245. Correction must then be applied for the diamagnetism of the various atoms and radicals and for the underlying diamagnetism of the central cobalt ion itself. The value of this correction, α, is computed from the following data by applying the Pascal formula : $\alpha = \Sigma\chi_A + \lambda$, where $\Sigma\chi_A$ represents the sum of the susceptibilities of all the atoms or radicals in the molecule and λ is a constitutive correction constant depending on the nature of the chemical bond involved.

	Cl.	NO$_3$.	NO$_2$.	NH$_3$.	H$_2$O.
$-\chi_A \times 10^6$	21	19	13·6	15	13·5

It follows from investigations by Rosenbohm (*Z. physikal. Chem.*, 1919, **93**, 693) that the value of λ is constant for each kind of ammine and is equal to $+ 60 \times 10^{-6}$ for all pentammines. The value of the total correction to be applied in the present case is $+ 72 \times 10^{-6}$, which is also that found experimentally by Rosenbohm for the diamagnetic susceptibility of the very similar compound $[Co(NH_3)_5NO_2]Cl_2$.

Variation of magnetic susceptibility with temperature. In the following table, χ_c is the susceptibility per gram-ion of cobalt corrected as explained before for the diamagnetism of the molecule.

T (K.).	$\chi_1 \times 10^6$.	$\chi_m \times 10^6$.	$\chi_c \times 10^6$.	$1/\chi_c$.	T (K.).	$\chi_1 \times 10^6$.	$\chi_m \times 10^6$.	$\chi_c \times 10^6$.	$1/\chi_c$.
70°	12·04	2949	3021	331	289°	4·10	1004	1076	929
89	10·44	2557	2629	380	290	3·90	955	1027	973
193	5·85	1433	1505	664	348·1	3·34	818	890	1123
284	4·21	1031	1103	907					

If the reciprocal, $1/\chi_c$ of the ionic susceptibility is plotted against the absolute temperature, a straight line is obtained. The variation of susceptibility follows a Curie–Weiss law $\chi_c(T + \Delta) = C$. We have for each experimental point the relation $1/\chi_c = T/C + \Delta/C$. The values of C and Δ have been calculated by application of the principle of least squares to this set of relations, and found to be $C = 0\cdot351$, $\Delta = 39\cdot9$. If we calculate the Weiss magneton number as defined by the relation, $\mu_W = 14\cdot07\sqrt{C}$, we find $\mu_W = 8\cdot32$. For this substance at 29° Râry and Bhar (*loc. cit.*) record a value of 13·9 Weiss magnetons. They state, however, " that we did not take sufficient pains to obtain magnetically pure samples in all cases, especially in the case of certain unstable compounds." We have carried out determinations on a number of samples prepared at different times and they gave concordant results. As the Weiss magneton lacks theoretical significance, it is preferable to express the result in Bohr magnetons which, on the " spin only " rule, is given by the relationship 8·6 Weiss magnetons $= 1\cdot73$ Bohr magnetons $=$ the moment produced by one unpaired spin. The observed magnetism of this black compound is

difficult to interpret, for although cobaltic salts are diamagnetic, yet cobaltous compounds usually possess moments greater than that predicted for an electron spin of $\frac{3}{2}$, *viz.*, $\mu_{eff.} = 3\cdot87$ Bohr magnetons (Sugden and Barkworth, *Nature*, 1937, **139**, 375). The complicating feature in this instance is the nitric oxide molecule and it seems preferable to defer discussion of this interesting case till more data, relating to similar substances, are available.

Nitrate. Experiments at room temperature and with air as surrounding medium show that nitrosopentamminocobalt nitrate is diamagnetic. Two experiments were made which gave the values $\chi_1 = -0\cdot19 \times 10^{-6}$ and $-0\cdot11 \times 10^{-6}$ for the gram-susceptibility.

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