The Co–N Bond Lengths in Co^{II} and Co^{III} Hexammines

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THE lengths of the Co–N bonds in Co^{II} and Co^{III} complexes are often quoted[1,2] as 2·5 and 1·9 Å, respectively, on the basis of early structure determinations, by powder methods, of $Co(NH_3)_6X_2$ (X = Cl, Br, I) and $Co(NH_3)_6I_3$.[3] This difference of 0·6 Å in the Co^{II}–N and Co^{III}–N bond lengths has been used to explain the slow rate of electron transfer reactions for Co^{II}–Co^{III} systems compared with other systems (*e.g.*, Fe^{II}–Fe^{III}). Since the decrease of ionic radius with increasing charge on the metal is small (perhaps 0·1 Å or less[4]), this difference in the Co^{II}–Co^{III} case has been ascribed to the change in spin, for Co^{II} complexes are usually high-spin and Co^{III} complexes low-spin. There is some recent evidence that this difference of 0·6 Å is unrealistic. Thus Dunitz[5] has reported a Co^{II}–N distance of 2·14 Å in bispyridylcobalt dichloride, and this value is more in keeping with Co^{III}–N bond {*e.g.*, 1·97 Å in $[N_3Co(NH_3)_5](N_3)_2$}.[6] Yet this comparison may not be a valid one owing to differences in the ligands. For this reason we have examined Co^{II} and Co^{III} hexammine halides.

The dichloride of hexamminecobalt(II) was chosen to ensure maximum accuracy in the Co–N bond-length determination. The trichloride and tribromide of hexamminecobalt(III) turn out to be monoclinic, with no crystallographic symmetry conditions on the hexamminecobalt ion. For this reason, the tri-iodide, which is cubic, was examined.

Both analyses were carried out using standard single-crystal film methods. The compounds crystallize in space group *Fm3m* of the cubic system. The dichloride has the K_2PtCl_6 structure whereas the tri-iodide has the $(NH_4)_3AlF_6$ structure. [In each, Co is in position (4*a*), N in position (24*e*). In the dichloride Cl is in (8*c*), in the tri-iodide I is in (8*c*) and in (4*b*).] If one neglects possible contributions of hydrogen atoms then both structure determinations involve the determination of just one positional parameter, that of the nitrogen atom. The results of the studies are shown in the Table.

The studies have thus shown that the difference between the two Co–N bond lengths is only 0·15 Å. Presumably arguments based on factors other than the bond-length difference must be used to explain the slow rates of electron transfer. More important, the results provide evidence that the effect of spin type (or more properly of the number of electrons in antibonding orbitals) on the metal radius is very small. Finally, the structure analyses are consistent with the n.m.r. evidence on the Co^{III} complex[7] that the hydrogen atoms are not occupying ordered positions at room temperature.

TABLE

	$Co(NH_3)_6Cl_2$	$Co(NH_3)_6I_3$
Method	Least-squares	Least-squares
Cell constant	10·122Å	10·82 Å
No. of observations	55	105
Reliability factor, *R*	7·7%	6·6%
N Parameter	0·2088 ± 0·0005	0·1805 ± 0·0017
Co–N Distance	2·114 ± 0·009 Å	1·96 ± 0·02 Å

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