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The Ring Conformation *d*-Electron Optical Activity of a Cyclic Triamine Cobalt(III) Complex

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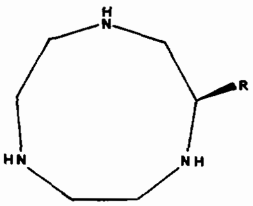
The synthesis of the ligand R(–)-2-methyl-1,4,7-triazacyclononane and its cobalt(III) complex [Co(R-MeTACN)$_2$]$^{3+}$ is reported. The complex is found to exhibit in the 480 nm region the largest ring-conformation d-electron optical activity yet recorded for the [CoN$_6$] chromophore, due to a chiral puckering, with the λ-conformation, of each of the six chelate rings. The c.d. spectrum of the complex is found to be consistent with the dynamic coupling model of d-electron optical activity, but not with the corresponding crystal field model.

Introduction

The *d*-electron optical activity of chiral diamine and polyamine complexes of the transition metal ions derives from two principal sources, firstly, a dissymmetric puckered conformation of the chelate ring or rings and, secondly, a chiral mutual disposition of the mean planes of two or more chelate rings. For equivalent diamine chelate rings the first contribution to the optical activity, the ring conformation effect, is approximately additive over the number of rings, whereas the second contribution, the mean-plane configurational effect, is proportional to the number of ring–ring interactions[1]. Both of these relations are quantitatively accommodated by a ligand-polarisability model for the *d*-electron optical activity of dihedral metal complexes, dependent upon dynamic Coulombic coupling between induced dipoles in the ligand groups and the leading electric multipole moment of the metal ion transition[2].

Further investigations of the model require a separation of the two principal contributions to the *d*-electron optical activity which, in the dihedral tris-diamine complexes of cobalt(III), are generally coexistent. Recently the synthesis of the bis-(1,4,7-triazacyclononane) complex of cobalt(III) has been reported[3], the triamine ligand TACN (I) being prepared by the method[4] of Peacock and Dutta.



I R = H
II R = Me

Models of the complex [Co(TACN)$_2$]$^{3+}$ suggest that the individual chelate rings of each ligand have a preferred common conformation, the ligand in the complex assuming either the ($\lambda\lambda\lambda$) or the ($\delta\delta\delta$) ring conformation set when spanning a triangular octahedral face. The mean-plane configurational effect is absent in the complex [Co(TACN)$_2$]$^{3+}$ and an optical isomer of the complex is expected to owe its *d*-electron optical activity to the effect arising from six chelate rings with a common ring conformation.

In order to avoid the probable statistical predominance of the *meso* form of [Co(TACN)$_2$]$^{3+}$ and the optical lability of the chiral forms we have prepared the analogous complex from R-(–)-2-methyl-1,4,7-triazacyclononane, R-MeTACN (II). The triamine ligand (II) was synthesised from the ditosylate of R-(–)-propylenediamine and the tritosylate of diethanolamine by Richman and Atkins procedure[5], which affords yields superior to those of the earlier method[4].

Experimental

R-2-methyl-1,4,7-triazacyclononane Trihydrobromide

R-(–)-propylenediamine (50 mmol), resolved by the method of Dwyer and coworkers[6], was converted to the ditosylate by treatment with two equivalents of *p*-toluene sulphonyl chloride in dry pyridine, and then into the corresponding disodium salt with sodium ethoxide in ethanol. The salt dissolved in DMF (500 ml) was maintained at 100° C for two hours during which time 50 mmol of the tritosylate of diethanolamine in DMF (250 ml) was added with stirring. The tritosylate of R-MeTACN (II) was precipitated from the cooled solution by the addition of water in 60% yield (20 g). Detosylation was effected in lower yield (*ca.* 10%) by refluxing the tritosylate for two days in mixture of glacial acetic acid (360 ml) and 47% aqueous hydrogen bromide (640 ml). Reduction of the volume to 100 ml followed by the addition of ether afforded a crystalline precipitate of R-MeTACN·3HBr.

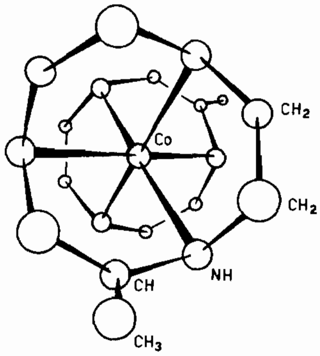
[Co(R-MeTACN)$_2$]I$_3$·2H$_2$O

Air was bubbled through a solution of R-MeTACN·3HBr (2 mmol), cobalt(II) bromide monohydrate (1 mmol) and sodium hydroxide (5 mmol) in water (5 ml) for ~ 30 minutes when yellow crystals of [Co(R-MeTACN)$_2$]Br$_3$ separated from the red solution, which contained the mono-R-MeTACN complex. The tribromide was converted by ion-exchange to the corresponding triiodide, which was precipitated from aqueous solution with ethanol, in which the mono-complex is soluble. Recrystallisation from water gave yellow hexagonal plates, analysing for [Co(R-MeTACN)$_2$]I$_3$.

The p.m.r. spectrum of [Co(R-MeTACN)$_2$]Cl$_3$ in DMSO-d$_6$ had the expected form, the shifts (and relative areas) being, CH$_3$ at 9.3 τ (3), CH$_2$ and CH at 7.7 τ (11), and NH at 4.2 τ (3).

Results and Discussion

The electronic absorption and c.d. spectrum of [Co(R-MeTACN)$_2$]$^{3+}$ (III), measured as the perchlorate salt in aqueous solution (Figure), shows a strong positive rotational strength associated with the magnetic-dipole allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ octahedral *d*-electron transition near 21 kK.



III

An overall positive rotational strength in this frequency region is characteristic of puckered five-membered chelate rings with the λ-conformation in complexes containing the [CoN$_6$] chromophore but devoid of the configurational dissymmetry arising from the chiral disposition of two or more chelate rings, such as the R-(–)-propylenediamine complex[7], *trans*-[Co(R-pn)$_2$(NH$_3$)$_2$]$^{3+}$, or the corresponding R,R-(–)-*trans*-1,2-diaminocyclohexane complex[8], *trans*-[Co(R,R-chxn)$_2$(NH$_3$)$_2$]$^{3+}$. The rotational strength of [Co(R-MeTACN)$_2$]$^{3+}$ at 21 kK is substantially larger (+0.145 Debye magneton) than that expected on an additive basis for six five-membered diamine chelate rings with the λ-conformation (+0.057 Debye-magneton) from the data given[8] for *trans*-[Co(R,R-chxn)$_2$(NH$_3$)$_2$]$^{3+}$, suggesting that each chelate ring of R-MeTACN has a synergistic effect upon the distortions from regular octahedral coordination produced by the other two chelate rings, on account of the cyclic structure of the tridentate ligand. The preliminary results of a X-ray diffraction analysis of the crystal and molecular structure of [Co(R-MeTACN)$_2$]I$_3$ show that each chelate ring of the complex has the λ-conformation and indicate that the [CoN$_6$] chromophore is elongated along the threefold rotational axis[9]. The angle between a Co–N bond and the C$_3$ axis is 51.6°, compared with the corresponding angle of 54.75° for regular octahedral coordination[9].

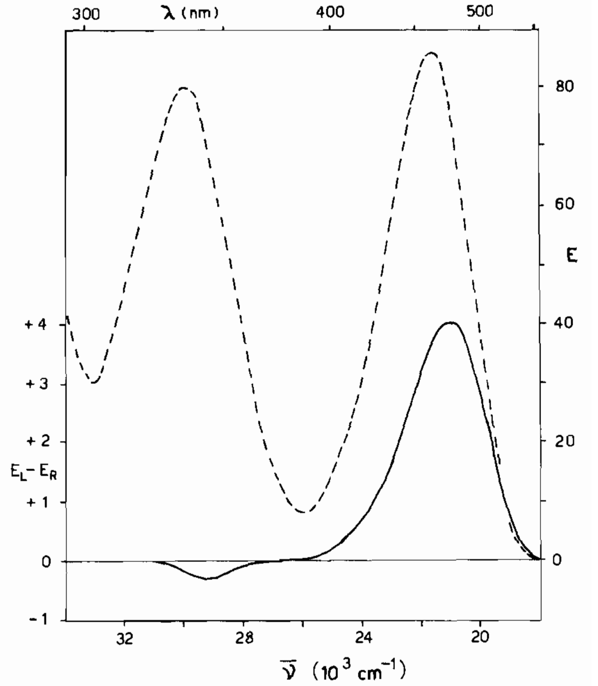
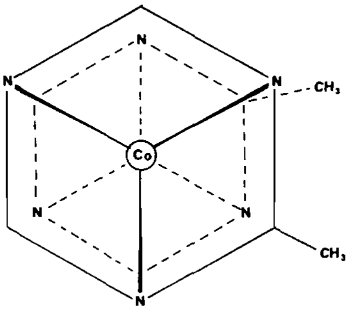


Figure. The absorption (upper curve) and c.d. spectrum (lower curve) of [Co(R-MeTACN)$_2$](ClO$_4$)$_3$ in water.

Despite the trigonal distortion produced by the axial elongation, the c.d. spectrum of [Co(R-MeTACN)$_2$]$^{3+}$ shows no sign of a trigonal splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ octahedral transition (Figure), in contrast to the cases of *trans*-[Co(R-pn)$_2$(NH$_3$)$_2$]$^{3+}$ and *trans*-[Co(R,R-chxn)$_2$(NH$_3$)$_2$]$^{3+}$ where a tetragonal splitting of the corresponding transition is evident in the respective c.d. spectra[7,8]. In the lack of an observed splitting of the 21 kK transition, and in other respects, [Co

(R-MeTACN)$_2$]$^{3+}$ resembles the recently-reported[10] complex of 1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane, (–)-*cis*-[Co(*cis,cis*-Metach)$_2$]$^{3+}$ (IV).



IV

In both complexes a tridentate ligand forming three virtually-equivalent chelate rings caps opposed triangular faces of the octahedron formed by the [CoN$_6$] chromophore. It is suggested[10] that (–)-*cis*-[Co(*cis, cis*-Metach)$_2$]$^{3+}$, like [Co(R-MeTACN)$_2$]$^{3+}$, is distorted from regular octahedral coordination by elongation along the C$_3$ rotation axis. The two complexes (III) and (IV) further resemble each other in displaying no observable c.d. band in the charge transfer region, 40 to 50 kK, whereas other chiral [CoN$_6$] complexes, including[7,8] *trans*-[Co(R-pn)$_2$(NH$_3$)$_2$]$^{3+}$ and *trans*-[Co (R,R-chxn)$_2$(NH$_3$)$_2$]$^{3+}$ exhibit a substantial c.d. absorption[1] ($|\Delta\varepsilon| > 10$). The absence of a trigonal splitting near 21 kK in the c.d. spectrum of (–)-*cis*-[Co (*cis,cis*-Metach)$_2$]$^{3+}$ is not wholly consistent with the use[10] of static crystal field sector rules[11] for the assignment of the absolute configuration of this complex, as the total rotational strength of the components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ octahedral transition vanishes in the crystal field theory if the trigonal splitting between those components is zero. The crystal field sector rules[11] are based upon second-order perturbation theory, one perturbation being a *gerade* static field, and the other an *ungerade* field, due to the substituents in the chiral molecular environment of the octahedral [CoN$_6$] chromophore. Both of the perturbations are required if the crystal field rotational strength, summed over the three components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ octahedral transition, is non-zero, and the *gerade* field necessarily produces an energy-splitting between those components.

In the alternative dynamic coupling theory no trigonal splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ octahedral transition is required for an observable optical activity in the 21 kK region of the spectrum of a chiral complex containing the [CoN$_6$] chromophore, and a non-zero total rotational strength for the transition emerges from a first-order, as well as a second-order, perturbational treatment[2]. According to the dynamic coupling model the leading electric multipole of the *d*-electron transition, a hexadecapole for each of the three components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the octahedral [CoN$_6$] chromophore, correlates Coulombically a transient induced electric dipole in each ligand group, such as NH$_2$ or CH$_2$, proportional to the polarisability of that group. The correlation gives a resultant electric dipole transition moment with a component collinear with the magnetic dipole moment of the *d*-electron transition, affording a non-zero rotational strength[2].

A qualitative application of the dynamic coupling model correlates the negative c.d. band of (–)-*cis*-[Co (*cis,cis*-Metach)$_2$]$^{3+}$ in the 20 kK region with the Λ-configuration (IV), as previously suggested[10], although on a more tenuous basis, from the static crystal field sector rules[11]. The dynamic coupling model further connects the substantial positive c.d. band of [Co(R-MeTACN)$_2$]$^{3+}$ near 21 kK (Figure) with the puckered λ-conformation of each of the six chelate rings (III), the crystal field sector rules being again of doubtful validity on account of the lack of an observed trigonal splitting.

The quantitative application of the dynamic coupling model requires a knowledge of the position of each atom or, at least, of the heavy atom in such groups as NH$_2$ or CH$_2$, in the coordinate frame of the chromophore[2]. The refinement of the crystal and molecular structure[9] of [Co(R-MeTACN)$_2$]I$_3$ is expected to provide the structural data required for a quantitative dynamic coupling treatment of the rotational strength of the complex ion (III) at 21 kK, which is the largest *d*-electron optical activity yet recorded due to chirally-puckered chelate rings.

Acknowledgments

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