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Infrared Spectroscopic Studies on the Conformation of $[M(en)_3]^{3+}$ Cations in the Solid State: Scope and Limitation

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Abstract

Twenty eight salts of (+), (–) or (±)-$[M(en)_3]^{3+}$ (M = Co, Cr), of known ring conformation, have been synthesised and their IR spectrum measured (KBr disc) in the 1100–700 cm^{-1} region.

Characteristic four-band patterns (1045, 1000, 890, 875 ± 5 cm^{-1}) were observed for simple salts with the lel_3 [$\Lambda(\delta\delta\delta)$, $\Delta(\lambda\lambda\lambda)$] conformation and this pattern was used in the assignment of chlorometalate salts with unknown conformations. Complexes with mixed ring conformations give more structured vibrational patterns, and the data are not sufficiently systematic to be used for conformational assignment. Any IR based conformational analysis in salts with oxyanions is less secure due to anion interference.

Introduction

Bidentate coordination of the 1,2-diaminoethane (en) ligand can result in two solid state conformations, λ and δ (Fig. 1). Thus, for a tris(1,2-diaminoethane) complex there are four solid state isomers (λλλ, λλδ, λδδ and δδδ) [1a]. The nomenclature of the $[M(en)_3]^{3+}$ system is complicated by the fact that the tris chelates can exist as optical isomers, Λ and Δ (Fig. 1). Consequently, racemic $M(en)_3^{3+}$ salts will normally crystallise with equal amounts of Λ and Δ enantiomers, each with the appropriate, enantiomeric, ring conformation *viz.* $\Lambda(\delta\delta\delta) \equiv \Delta(\lambda\lambda\lambda)$, $\Lambda(\delta\delta\lambda) \equiv \Delta(\lambda\lambda\delta)$, $\Lambda(\delta\lambda\lambda) \equiv \Delta(\lambda\delta\delta)$ and $\Lambda(\lambda\lambda\lambda) \equiv \Delta(\delta\delta\delta)$ (Table 1). While the above nomenclature is quite satisfactory for the separate (+)- or (–)-$[M(en)_3]^{3+}$ salts, it is cumbersome for racemates. Therefore, a chirality invariant nomenclature is often used for the four conformations in racemic systems, *viz.* lel_3, lel_2ob, $lelob_2$ and ob_3, where the C–C axis of the en ligand is parallel or oblique to the C_3 axis of the cation [1b]. Thus the $\Lambda(\delta\delta\delta) \equiv \Delta(\lambda\lambda\lambda)$ combination is represented by lel_3 and the $\Lambda(\lambda\lambda\lambda) \equiv \Delta(\delta\delta\delta)$ by ob_3 (Table 1).

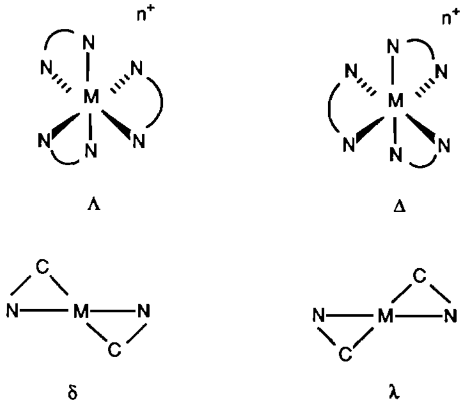

Fig. 1. Ring conformations and chiral forms in $[M(en)_3]^{n+}$ cations.

TABLE 1. Nomenclature Relationships for $[M(en)_3]^{n+}$ Cations

		N^a
$\Lambda(\delta\delta\delta) \equiv \Delta(\lambda\lambda\lambda)$	lel_3	23
$\Lambda(\delta\delta\lambda) \equiv \Delta(\lambda\lambda\delta)$	lel_2ob	3
$\Lambda(\delta\lambda\lambda) \equiv \Delta(\lambda\delta\delta)$	$lelob_2$	7
$\Lambda(\lambda\lambda\lambda) \equiv \Delta(\delta\delta\delta)$	ob_3	1

[a] Number of examples found for M^{n+} [30].

Molecular mechanics calculations of various sophistication indicate the $\Delta(\lambda\lambda\lambda)$ (lel_3) conformation is about 8 kJ mol^{-1} more stable than the $\Delta(\delta\delta\delta)$ (ob_3) for the gas phase ion, but the actual conformation adopted in the solid state depends on the nature of the anion.

To date, the ring conformations of at least 28 $[M(en)_3]^{3+}$ (M = Co, Cr) complexes have been determined directly or indirectly by single crystal X-ray analysis in the solid state (Table 2). Similar information is also available for a considerable number of $[M(en)_3]^{n+}$ salts with other central metal ions [30].

One technique that has the potential to yield comparative solid state structural information is infrared spectroscopy and this has been applied to

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TABLE 2. $[M(en)_3]^{3+}$ Salts (M = Co, Cr) of Known Ring Conformation

Salt	ρ_{lit} (g cm^{-3})	ρ_{meas} [a] (± 0.01 g cm^{-3})	Characteristic IR bands[a] (± 2 cm^{-1})	Reference
lel_3, $\Lambda(\delta\delta\delta)$ or $\Delta(\lambda\lambda\lambda)$				
(±)-$[Co(en)_3]Cl_3 \cdot 2.8H_2O$	1.493	1.472	1050, 1002, 895, 881	2
(+)-Λ-$[Co(en)_3]Cl_3$	1.585	1.585	1050, 1000, 895, 883	3, 4
(±)-$[Cr(en)_3]Cl_3 \cdot 3H_2O$	1.449	1.469	1047, 1001, 882, 868	2
(+)-Λ-$[Cr(en)_3]Cl_3 \cdot 2H_2O$	1.417	1.42	1041, 1002, 884, 868	5
(±)-$[Co(en)_3]Br_3$			1045, 999, 893, 879	6
(+)-Λ-$[Co(en)_3]Br_3 \cdot H_2O$	1.811	1.886	1048, 999, 893, 880	7
(±)-$[Co(en)_3](NCS)_3$	1.534	1.484	1047, 1001, 883, 874	8
(+)-Λ-$[Co(en)_3](NCS)_3$			1040, 1002, 885, 875	9
(+)-Λ-$[Co(en)_3](NO_3)_2$[c]	1.756	1.758		10
(±)-$[Co(en)_3][Fe(CN)_6]$	1.54	1.539	1040, 994, 889, 871	11
(±)-$[Co(en)_3]_2[CdCl_6]Cl_2$	1.815	1.82	1044, 999, 896, 887	12
(±)-$[Co(en)_3]_2[HPO_4]_3 \cdot 9H_2O$[c]	1.65	1.606		13
(−)-Δ-$[Co(en)_3][MoO_3(ox)(OH_2)]I \cdot 2H_2O$	2.086			14
(±)-$[Cr(en)_3]_2[HgCl_4]_3$	2.16	2.26	1038, 991, 873, 860	15
(+)-Λ-$[Co(en)_3][(+)\text{-}T]Br \cdot 0.5H_2O$[b, c]				16
(+)-Λ-$[Co(en)_3][(+)\text{-}T]Cl \cdot 0.5H_2O$[b, c]	1.567	1.577		17
Li-(+)-Λ-$[Cr(en)_3][(+)\text{-}T]_2$[b, c]	1.54	1.60		16
lel_2ob, $\Lambda(\delta\delta\lambda)$ or $\Delta(\lambda\lambda\delta)$				
(±)-$[Co(en)_3]_2[Pb_2Cl_9]Cl$	2.25	2.33	1043, 996, 930, 884, 876	18
(+)-Λ-$[Cr(en)_3]Br_3 \cdot 0.6H_2O$	1.811	1.767	1045, 997, 930, 878, 867	19
$lelob_2$, $\Lambda(\delta\lambda\lambda)$ or $\Delta(\lambda\delta\delta)$				
(±)-$[Co(en)_3][HgCl_3I]Cl$	2.67	2.60	1050, 1040, 1012, 997, 980, 890, 878, 871	15
(±)-$[Co(en)_3]I_3 \cdot H_2O$	2.343	2.284	1043, 1013, 996, 890, 869	20
(±)-$[Cr(en)_3]I_3$	2.301	2.37	1045, 1033, 998, 881, 863	21
(+)-Λ-$[Cr(en)_3](NCS)_3$	1.471	1.47	1045, 1001, 992, 959, 922, 878, 871, 862	22
(−)-Δ-$[Cr(en)_3](NCS)_3$	1.471	1.46	1040, 1001, 998, 932, 878, 867	23
(±)-$[Co(en)_3][SnCl_3]Cl$	1.992	1.884	1045, 1025, 996, 912, 891, 883	24
(±)-$[Co(en)_3][Cu_2Cl_8]Cl_2$	1.862	1.727	1061, 1055, 1030, 1010, 995, 904, 888, 868	25
(±)-$[Co(en)_3][Cr(CN)_5NO]$	1.58	1.58	1045, 999, 893, 886, 871	26
Miscellaneous				
(±)-$[Cr(en)_3](NCS)_3 \cdot 0.75H_2O$ lel_2(0.7 lel, 0.3 ob)	1.397	1.396	1037, 1010, 998, 924, 877, 865	27, 28
(±)-$[Cr(en)_3][Ni(CN)_5]$ lel_2ob, $lelob_2$	1.55	1.546	1058, 1019, 1000, 888, 880, 874	29

[a] This research. [b] T = tartrate (−2) anion. [c] Characteristic bands distorted by anion absorptions.

$[M(en)_3]^{n+}$ systems by previous workers [31–33] over a limited range of complexes.

If such a technique were successful, it would considerably simplify the assignment of ring conformations in the solid state. Nevertheless, it is doubtful if this technique, even with the most sophisticated instrumentation, could provide structural information on disordered ring conformations [27, 28, 34] or systems where two independent cations, with different conformations coexist in the same lattice [29, 35], as has been found by crystallography.

Despite this, however, it may be possible using IR techniques to provide patterns that eliminate the common Λ(δδδ), Δ(λλλ) (lel_3) type and leave the more complicated examples for single crystal X-ray analysis.

This is the situation we have reached after measuring the IR spectrum of $[M(en)_3]^{3+}$ salts of known conformation and several with unknown conformations (Table 3).

Experimental

Salts of (+)-, (−)- and (±)-$[M(en)_3]^{3+}$ (M = Co, Cr) with known crystal structures were prepared by the literature methods (Table 2). These were

TABLE 3. IR Spectra and Conformational Assignments for Chlorometalate Salts of [M(en)$_3$]$^{3+}$ (M = Co, Cr)[a]

Salt	IR frequencies
	Assigned to lel$_3$ or Δ(λλλ)
(±)-[Co(en)$_3$][Al$_x$Cl$_y$]	1049, 1001, 894, 879
(±)-[Co(en)$_3$][Fe$_x^{III}$Cl$_y$]	1055, 1002, 901, 887
(±)-[Co(en)$_3$][Mn$_x$Cl$_y$]	1049, 1002, 895, 881
(±)-[Co(en)$_3$][Sr$_x$Cl$_y$]	1050, 1002, 895, 881
(±)-[Co(en)$_3$][Ag$_x^{I}$Cl$_y$]	1048, 998, 893, 883
(–)-Δ-[Co(en)$_3$]Cl$_3$	1053, 1005, 898, 886
(–)-Δ-[Cr(en)$_3$]Cl$_3$	1055, 1009, 891, 879
	Unknown conformation
(+)-Λ-[Co(en)$_3$]I$_3$	1045, 1021, 993, 890, 876
(±)-[Cr(en)$_3$]Br$_3$	1044, 1008, 999, 881, 868
(±)-[Co(en)$_3$][HgCl$_5$][b]	1050, 1006, 993, 891, 881, 873
(±)-[Co(en)$_3$][CoCl$_4$]Cl[c]	1047, 1026, 1013, 999, 893, 882, 870
(±)-[Co(en)$_3$][ZnCl$_4$]Cl[c,d]	1047, 1030, 1015, 997, 892, 880, 872
(±)-[Co(en)$_3$][Sb$_x^{V}$Cl$_y$]	1047, 1019, 997, 895, 889, 881
(±)-[Co(en)$_3$][Cu$_x^{I}$Cl$_y$]	1050, 1030, 1010, 1002, 895, 889

[a]The stoichiometry of several of these salts is uncertain. [b]Calc. for [Co(en)$_3$][HgCl$_5$]: C, 11.68; H, 3.92; N, 13.62. Found: C, 11.80; H, 4.36; N, 13.61% but it is unwise to assume any particular stereochemistry for the Hg(II) atom [15]. [c]These salts are probably isomorphous. [d]By analogy with the corresponding hexaammine salts [36, 37].

characterised by comparing the measured flotation density (±0.01 g cm^{-3}) with that cited in the literature (often calculated from the cell parameters) (Table 2).

Salts of unknown conformation (Table 3) were mainly prepared with complex chloro anions from (+)-, (–)- and (±)-[M(en)$_3$]Cl$_3$ (M = Co, Cr and M′Cl$_x^{n-}$ in HCl [M′ = Mn(II), Al(III), Fe(III), Sr(II), Ag(I), Cu(I), Sb(V), Hg(II), Zn(II), Co(II)]. The composition of the resulting chloro anion depends on the HCl concentration and Jorgensen's compilation [38] was used as a guide. The general procedure was to add (+)-, (–)- or (±)-[M(en)$_3$]Cl$_3$·nH$_2$O (3 g) in water (100 ml) to 6 g of M′Cl$_x$ in 6 or 12 M HCl (100 ml), both at 60 °C and to collect the resulting product in crops over several weeks at room temperature. Proportionately smaller quantities were used for the chiral cations, and the Cr(III)-containing solutions were protected from light.

Infrared spectra were measured (KBr disc) using a Shimadzu IR-27G recording instrument calibrated with polystyrene. Spectra were recorded over the 4000–400 cm^{-1} range and from 1100–700 cm^{-1} using the X5 scale expansion. Several different concentrations were used for each sample to give peak frequencies accurate to ±2 cm^{-1}.

Results and Discussion

Salts of [M(en)$_3$]$^{3+}$ cations with the lel$_3$, Λ(δδδ) or Δ(λλλ) conformation generally give a characteristic four band pattern in the C–C stretch and en ring bending mode region of the infrared spectrum (1045, 1000, 890, 875 ± 5 cm^{-1}) (Fig. 2).

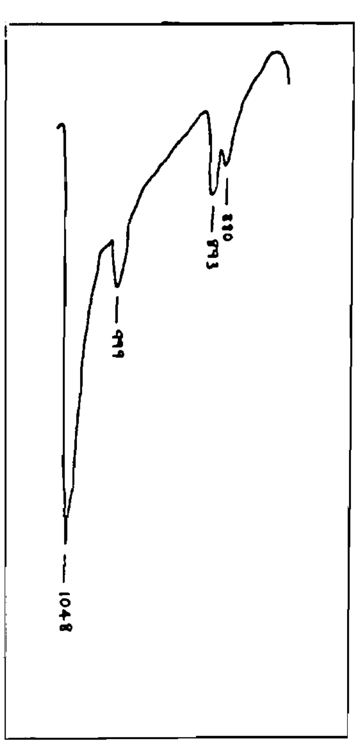

Fig. 2. Typical IR spectrum (KBr disc, 1100–700 cm^{-1}) of a simple salt of [M(en)$_3$]$^{3+}$ in the lel$_3$, Λ(δδδ) or Δ(λλλ) conformation: (+)-Λ-[Co(en)$_3$]Br$_3$.

With cations containing mixed ring conformations, the band patterns in this region are more complex especially at the 890, 875 cm^{-1} doublet and at $\sim$1000 cm^{-1}. An additional band at $\sim$925 cm^{-1} often occurs (Table 2). Using this information, we are able to assign the lel_3 configuration to several chlorometalate (M′) salts (see 'Experimental') of (±)-$[\mathrm{Co(en)_3}]^{3+}$ [M′ = Mn(II), Al(III), Fe(III), Sr(II), Ag(I)] and the $\Delta(\lambda\lambda\lambda)$ configuration to (–)-$[\mathrm{M(en)_3}]\mathrm{Cl_3}$ [M = Co, Cr] while the ring conformations in (+)-$[\mathrm{Co(en)_3}]\mathrm{I_3}$, (±)-$[\mathrm{Cr(en)_3}]\mathrm{Br_3}$ and the $[\mathrm{Co(en)_3}]^{3+}$ chlorometalate salts of Hg(II), Sb(V), Cu(I), Zn(II) and Co(II) are almost certainly mixed (Table 3).

We have deliberately avoided unknown salts formed with oxyanions, as the intense IR absorption at 1400–1100 cm^{-1} will at least distort, and at worst completely obscure, the distinguishing band pattern characteristic of the ring conformation.

It is obvious from the data in Tables 2 and 3 that only occasionally do analogous $[\mathrm{M(en)_3}]^{3+}$ salts of Co(III) and Cr(III) have identical ring conformations although the number of comparisons is not large. When this is the case, however, the salts are usually isomorphous, e.g. (±)-$[\mathrm{M(en)_3}]\mathrm{X_3}\cdot n\mathrm{H_2O}$ (X = Cl, $n = 3$; X = Br, $n = 0$) [9]. One likely explanation for the difference is that the Co(III)–N distance (1.97 Å) is smaller than the Cr(III)–N distance (2.10 Å). This difference has been used to account for the lack of isomorphism in *mer*-$[\mathrm{MCl(en)(dpt)}]\mathrm{ZnCl_4}$ [M = Co(III), Cr(III)] where, in the Co(III) case, the six-membered rings are chair, twist; while for the entirely analogous Cr(III) complex the rings are chair, chair [39].

Our conclusions are that relatively unsophisticated IR instrumentation can provide important preliminary information on the ring conformations of suitable (non-oxyanion) salts of $[\mathrm{M(en)_3}]^{3+}$. In particular, if the appropriate four band pattern is observed in the 1100–700 cm^{-1} region, then the common lel_3, $\Lambda(\delta\delta\delta)$ or $\Delta(\lambda\lambda\lambda)$ arrangement can be confidently assigned.

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