

## Mixed-ligand Complexes of Trivalent Lanthanides. Part 3.† Complexes of Heptafluorodimethyloctane-3,5-dione and Pyrazine: Syntheses and Spectral Studies

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The lanthanide(III) tris(heptafluorodimethyloctanedionates),  $[\text{Ln}(\text{fod})_3]$ , form solid adducts with pyrazine (pyz) resulting in an increase in co-ordination number of the lanthanides from 6 to 7. In these adducts pyrazine co-ordinates through only one of its nitrogen atoms. The praseodymium, europium, and ytterbium adducts have been investigated for their applicability as lanthanide shift reagents. The dipolar shift produced in the spectra of butanol, benzyl alcohol, and dibutyl ether is discussed. The complexes do not dissociate even in the presence of added substrates (alcohols or ether).

Lanthanide  $\beta$ -diketonates<sup>1-11</sup> have been routinely used as lanthanide shift reagents (l.s.r.s) to simplify the n.m.r. spectra of organic compounds containing suitable heteroatoms,<sup>4,5</sup> to distinguish between *N*- and *S*-bonded thiocyanato-ligands,<sup>10</sup> and to study the rates of reactions.<sup>11</sup> We have previously investigated a number of mixed-ligand lanthanide complexes, containing oxygen and nitrogen donors, and interesting studies on the chemistry of these complexes and their ability as l.s.r.s have been reported.<sup>12-16</sup> Here we report a similar investigation of mixed-ligand complexes of most of the trivalent lanthanides (except Ce and Pm), yttrium and lanthanum with 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione (Hfod) and pyrazine (pyz) and n.m.r. spectral studies.

### Experimental

All the materials used were the same as described earlier.<sup>14,15</sup> The methods were also similar to those employed previously.<sup>14-16</sup> Some of the n.m.r. spectra are recorded on a JEOL JNM FX 100 FT spectrometer.

The lanthanide complexes with Hfod were synthesized by the method of Springer *et al.*<sup>2</sup> The mixed-ligand lanthanide complexes were synthesized by mixing  $[\text{Ln}(\text{fod})_3]$  and pyrazine in 1:1 molar ratio in ethanol. The mixture was refluxed for 1 h on a water-bath. The volume of the resulting solution was reduced to a minimum on a hot plate, followed by slow evaporation at room temperature. Repeated crystallization gave shiny crystals which were dried *in vacuo* over  $\text{P}_2\text{O}_5$  for several days.

### Results and Discussion

The  $[\text{Ln}(\text{fod})_3]$  chelates were allowed to react with pyrazine (1:1 ratio) which yielded mixed-ligand complexes of general formula  $[\text{Ln}(\text{fod})_3(\text{pyz})]$ , increasing the co-ordination number of the trivalent lanthanides from 6 to 7 (Table 1). These adducts are crystalline solids with sharp melting points. They are insoluble in non-polar solvents but are soluble in methanol, ethanol, and hot chloroform. The molar conductance ( $10^{-3}$  mol  $\text{dm}^{-3}$  solutions) in methanol revealed that the adducts are non-electrolytes<sup>17</sup> (Table 1).

In the complexes of pyrazine the low local symmetry experienced by the pyrazine moiety results in a strong band between

950 and 1000  $\text{cm}^{-1}$ .<sup>18</sup> All the complexes display a very strong band in this region (945–955  $\text{cm}^{-1}$ ), which is absent from the spectra of the chelates containing only fod. This suggests that pyrazine is co-ordinated through only one nitrogen. Another band appears in the region 2968–2976  $\text{cm}^{-1}$  which has been assigned to the hydrogen stretching of the pyrazine moiety. The out-of-plane hydrogen bending and out-of-plane ring-bending modes of pyrazine have shifted to higher frequencies and appear in the regions 808–822 and 420–450  $\text{cm}^{-1}$ , respectively.<sup>19</sup> A weak band appearing between 275 and 280  $\text{cm}^{-1}$  has been assigned to the metal–nitrogen frequency.<sup>15,16,20</sup> The i.r. absorptions of the chelates are also present in the spectra of the adducts, with their positions slightly shifted.

The thermal data for the complexes are given in Table 1. The thermograms are similar in shape with rapid weight losses (7.00–7.55%) between 210 and 240 °C, corresponding to the loss of one pyrazine molecule (theoretical weight loss 7.02–7.59%). Differential thermal analysis of the complexes reveals two strong endothermic peaks representing the melting point and expulsion of pyrazine, respectively. The i.r. spectra of complexes heated to 240 °C do not show bands characteristic of pyrazine. All the evidence indicates that pyrazine has co-ordinated to the lanthanides.

*N.M.R. Spectra.*—The n.m.r. spectra of the complexes have been recorded in  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{SO}$ . The corresponding data are summarized in Table 2. The signals of the fod appear at 1.11–1.15 and 6.10–6.15 p.p.m. for the *t*-butyl and methine protons, respectively, as relatively sharp singlets, in the case of the diamagnetic adducts. The spectrum of a  $\text{CDCl}_3$ – $\text{CCl}_4$  solution of pyrazine gives only one signal at 8.50 p.p.m. The adducts display two comparatively broad signals, one at low field and the other at high field as compared to free pyrazine. The protons  $\text{H}^2$  and  $\text{H}^6$  nearest to the nitrogen through which co-ordination has occurred are shifted to high field and the other two ( $\text{H}^3$  and  $\text{H}^5$ ) appear at lower field due to deshielding. In the spectra of the paramagnetic adducts, the pyrazine protons displayed large shifts as compared to the diamagnetic adducts, indicating considerable delocalization of unpaired electron density into the aromatic ligand. The shift is predominantly of pseudo-contact origin since the  $g$  tensor is anisotropic. The dipolar shift is limited by the geometry of the complex species [equation (1)]<sup>21</sup> and the role of angle  $\theta$  in

$$\Delta\nu/\nu_0 = -D[(3\cos^2\theta - 1)/R^3] \quad (1)$$

† Part 2 is ref. 16.

**Table 1.** Elemental analyses and some characterizing data

Complex	Colour	M.p. (°C)	Analysis (%) <sup>a</sup>				$\Lambda_M/\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup>	$\mu_{\text{eff}}$	Weight loss (%) due to pyrazine <sup>a,b</sup>	
			Metal	C	H	N				
[Y(fod) <sub>3</sub> (pyz)]	White	98	8.50 (8.45)	37.35 (38.70)	3.30 (3.25)	2.65 (2.65)	10.9	<i>c</i>	7.50 (7.59)	[230]
[La(fod) <sub>3</sub> (pyz)]	White	135	12.50 (12.60)	36.85 (36.95)	3.10 (3.05)	2.55 (2.55)	22.4	<i>c</i>	7.00 (7.25)	[210]
[Pr(fod) <sub>3</sub> (pyz)]	Green	141	12.15 (12.75)	36.50 (36.90)	3.10 (3.05)	2.45 (2.55)	16.3	3.59	7.55 (7.23)	[236]
[Nd(fod) <sub>3</sub> (pyz)]	Violet	145	13.10 (13.00)	37.00 (36.80)	3.05 (3.05)	2.55 (2.50)	15.8	3.80	7.50 (7.21)	[224]
[Sm(fod) <sub>3</sub> (pyz)]	Light yellow	123	13.50 (13.50)	37.65 (36.60)	3.00 (3.05)	2.60 (2.50)	—	2.44	7.00 (7.17)	[232]
[Eu(fod) <sub>3</sub> (pyz)]	Light yellow	138	13.50 (13.60)	36.20 (36.55)	3.00 (3.05)	2.50 (2.50)	12.4	3.70	7.50 (7.16)	[230]
[Gd(fod) <sub>3</sub> (pyz)]	White	180	14.00 (14.00)	36.85 (36.35)	3.15 (3.05)	2.50 (2.50)	—	8.01	7.50 (7.13)	[240]
[Tb(fod) <sub>3</sub> (pyz)]	Dirty white	168	14.20 (14.15)	36.40 (36.30)	2.90 (3.05)	2.55 (2.50)	10.5	9.81	7.50 (7.13)	[240]
[Dy(fod) <sub>3</sub> (pyz)]	White	165	14.40 (14.40)	36.50 (36.20)	3.15 (3.00)	2.45 (2.50)	—	10.40	—	—
[Ho(fod) <sub>3</sub> (pyz)]	Yellow	148	14.80 (14.60)	36.15 (36.16)	3.05 (3.00)	2.60 (2.50)	11.6	10.70	—	—
[Er(fod) <sub>3</sub> (pyz)]	Pink	120	14.70 (14.75)	36.85 (36.05)	3.05 (3.00)	2.50 (2.45)	13.8	9.48	—	—
[Tm(fod) <sub>3</sub> (pyz)]	White	105	15.00 (14.90)	35.40 (36.00)	3.05 (3.00)	2.45 (2.45)	13.9	7.40	—	—
[Yb(fod) <sub>3</sub> (pyz)]	White	103	15.00 (15.20)	36.00 (35.85)	2.95 (3.00)	2.55 (2.45)	17.6	4.60	7.50 (7.03)	[210]
[Lu(fod) <sub>3</sub> (pyz)]	Dirty white	113	15.30 (15.35)	35.70 (35.80)	3.05 (3.00)	2.45 (2.45)	18.1	<i>c</i>	7.50 (7.02)	[225]

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Temperatures (°C) in square brackets. <sup>c</sup> Diamagnetic.

**Table 2.** N.m.r. spectral data<sup>a</sup>

Compound	Pyrazine		Diketone	
	H <sup>2</sup> , H <sup>6</sup>	H <sup>3</sup> , H <sup>5</sup>	CH	Bu <sup>t</sup>
(1) Pyrazine		8.50 <sup>b</sup>	—	—
(2) [Y(fod) <sub>3</sub> (pyz)]	8.83	4.17	6.12	1.11
(3) [Lu(fod) <sub>3</sub> (pyz)]	9.05	4.45	6.13	1.13
(4) [Pr(fod) <sub>3</sub> (pyz)]	-4.60 <sup>c</sup>	11.82	<i>d</i>	-0.62 <sup>c</sup>
(5) [Eu(fod) <sub>3</sub> (pyz)]	16.88	6.43	1.55	1.20
(6) [Yb(fod) <sub>3</sub> (pyz)]	35.25	16.92	-20.07 <sup>c</sup>	1.82

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub>-(CD<sub>3</sub>)<sub>2</sub>SO. Chemical shifts in p.p.m. downfield relative to internal SiMe<sub>4</sub>. <sup>b</sup> Sharp singlet. <sup>c</sup> Chemical shift in p.p.m. upfield relative to internal SiMe<sub>4</sub>. <sup>d</sup> Not observed.

changing its sign is immediately obvious from the spectrum of [Pr(fod)<sub>3</sub>(pyz)] (**4**) only where the resonances of H<sup>2</sup> and H<sup>6</sup> are shifted to high field of SiMe<sub>4</sub> (-4.60 p.p.m.).

An additional feature observed is the broadening of the ring-proton resonances and absence of coupling of these nuclei, even in the case of [Eu(fod)<sub>3</sub>(pyz)] (**5**), because of paramagnetically enhanced relaxation of these nuclei.<sup>14</sup> The resonances of complex (**5**) are narrower than those of (**4**) and (**6**), owing to the low-energy first excited state of Eu<sup>3+</sup>, which in turn results in a short electron relaxation time. N.m.r. studies of paramagnetic [Ln(dpm)<sub>3</sub>] (dpm = 2,2,6,6-tetramethylheptane-3,5-dione) and Ln(fod)<sub>3</sub> chelates and their adducts have been biased heavily towards the t-butyl resonance;<sup>7,22</sup> to our knowledge the

methine resonance has not been reported, except for europium and terbium tris(acetylacetonates).<sup>1</sup> The methine resonance in complexes (**5**) and (**6**) is greatly shifted to high field as compared to the diamagnetic analogues. For (**6**) it appears at -20.07 p.p.m., but for (**4**) it is not observed at all.

One of the objects of this study was to examine applicability of the paramagnetic complexes as l.s.r.s. The praseodymium (**4**), europium (**5**), and ytterbium (**6**) complexes have been tested with three organic substrates, namely butanol (A), benzyl alcohol (B), and dibutyl ether (C). The induced paramagnetic shifts are summarized in Tables 3—5. In the absence of the polar solutes, these adducts exhibit a solubility of 20—25 mg per 0.5 cm<sup>3</sup> CDCl<sub>3</sub>. However, upon addition of 7.4—13.0 mg of any one of the substrates studied (yield a 0.2 mol dm<sup>-3</sup> solution in 0.5 cm<sup>3</sup> CDCl<sub>3</sub>) an approximately five-fold increase in the solubility is noted, permitting the dissolution of an equimolar amount (110—114 mg) of the complexes.

The t-butyl resonance of a pure paramagnetic complex in CDCl<sub>3</sub> with reference to the diamagnetic case {[Y(fod)<sub>3</sub>(pyz)] 1.10 p.p.m.} shifts slightly to high field as the concentration is increased. In the presence of the complexing substrates, the t-butyl and pyrazine resonances are more strongly shifted from the diamagnetic position, the magnitude of the shift being approximately correlated with the relative shift power of the complex. For example, the t-butyl resonance of 0.2 mol dm<sup>-3</sup> complex (**5**) in CDCl<sub>3</sub> occurs at 1.2 p.p.m. (Table 2) but on addition of substrate A moves to 0.45 p.p.m. The resonances of the pyrazine moiety of the complex also move and appear at 4.62 and 22.27 p.p.m. for H<sup>3</sup>,H<sup>5</sup> and H<sup>2</sup>,H<sup>6</sup> protons, respectively. For complex (**4**) the t-butyl resonance is shifted to low field of SiMe<sub>4</sub> (1.15 p.p.m.) and the ring protons are also shifted to lower fields (H<sup>2</sup>,H<sup>6</sup> at -4.6, H<sup>3</sup>,H<sup>5</sup> at 20.57 p.p.m.). Similar effects are observed with complex (**6**). These observ-

**Table 3.** Paramagnetic shift in the spectrum of butanol<sup>a</sup>

Complex	OH	H <sub>α</sub>	H <sub>β</sub>	H <sub>γ</sub>	H <sub>δ</sub>
[Eu(fod) <sub>3</sub> (pyz)] <sup>b</sup>	<i>c</i>	9.57	5.60	3.92	1.92
[Pr(fod) <sub>3</sub> (pyz)] <sup>d,e</sup>	<i>c</i>	-18.77	-10.71	-7.43	-3.24
[Yb(fod) <sub>3</sub> (pyz)] <sup>d</sup>	107.73	36.18	20.71	13.30	6.84

<sup>a</sup> Shifts in p.p.m. downfield relative to internal SiMe<sub>4</sub>. <sup>b</sup> Spectrum recorded on a 60-MHz machine. <sup>c</sup> The shift is extremely large and was not recorded. <sup>d</sup> Spectrum recorded on a 100-MHz machine. <sup>e</sup> Shifts in p.p.m. upfield relative to internal SiMe<sub>4</sub>.

**Table 4.** Paramagnetic shift in the spectrum of benzyl alcohol<sup>a</sup>

Complex	OH	CH <sub>2</sub>	H <sub>o</sub>	H <sub>m</sub>	H <sub>p</sub>
[Eu(fod) <sub>3</sub> (pyz)] <sup>b</sup>	19.36	7.93	3.91	1.26	1.14
[Pr(fod) <sub>3</sub> (pyz)] <sup>c</sup>	-46.77 <sup>d</sup>	-15.28 <sup>d</sup>	6.10	2.38	2.07
[Yb(fod) <sub>3</sub> (pyz)] <sup>c</sup>	<i>e</i>	20.40	9.52	3.05	2.44

<sup>a</sup> Shifts in p.p.m. downfield relative to internal SiMe<sub>4</sub>. <sup>b</sup> Spectrum recorded on a 60-MHz machine. <sup>c</sup> Spectrum recorded on a 100-MHz machine. <sup>d</sup> Shift in p.p.m. upfield of internal SiMe<sub>4</sub>.

**Table 5.** Paramagnetic shift in the spectrum of dibutyl ether\*<sup>a</sup>

Complex	H <sub>α</sub>	H <sub>β</sub>	H <sub>γ</sub>	H <sub>δ</sub>
[Eu(fod) <sub>3</sub> (pyz)]	2.35	1.47	0.55	0.26
[Yb(fod) <sub>3</sub> (pyz)]	8.27	6.08	2.98	1.20

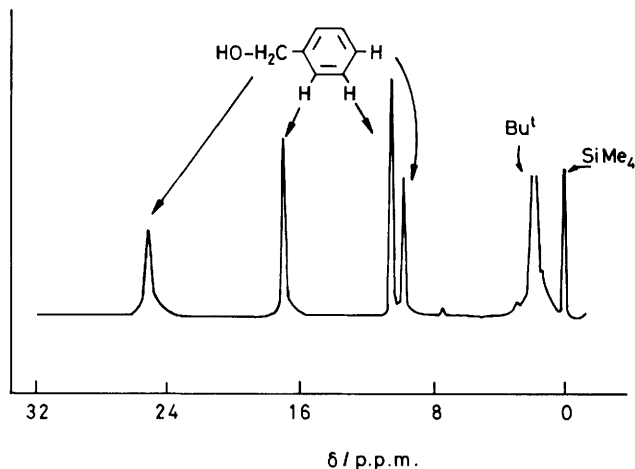
\* Shifts in p.p.m. downfield relative to internal SiMe<sub>4</sub>, recorded on a 60-MHz machine.

ations and the fact that the spectra of the substrates A—C are unaffected (except upon increasing concentration) by addition of any amount of the complexes show that the co-ordination of the complexes to the substrate occurs through the oxygen lone-pair electrons and can best be rationalized in terms of a change in the co-ordination geometry of the complexes upon association.<sup>2,3</sup>

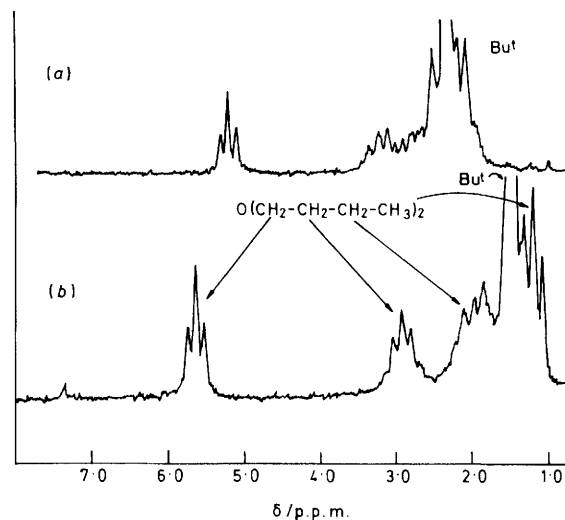
The effect on the resonance positions of the protons of substrate A upon addition of complex (4), (5), or (6) is shown in Table 3. In the absence of l.s.r. the two methylene protons coalesce and appear at 1.43 p.p.m. Upon addition of complex, the spectrum becomes amenable to a first-order analysis. Complex (5) shifts the signals downfield with respect to those of pure substrate A, whereas (4) shifts the whole spectrum to high field of SiMe<sub>4</sub>. Complex (6) produces larger shifts than (5) but at the expense of resolution.

In the spectrum of pure substrate B the ring protons resonate as a sharp singlet at 7.36 p.p.m. Upon addition of 100 mg of complex (5) the spectrum becomes first order; all ring protons are resolved, and greatly shifted downfield. The downfield shift induced by complex (6) is very large (Figure 1) and results in loss of the fine coupling, owing to the long electron relaxation time of ytterbium(III) as compared to europium(III). Complex (4) resulted in an upfield shift of the entire benzyl alcohol spectrum, but only the CH<sub>2</sub> (-10.68) and hydroxyl (-44.61) protons crossed the SiMe<sub>4</sub> envelope (for shifts see Table 4). This shows the importance of the angle term in changing the sign of the shift.

Finally experiments were carried out with dibutyl ether (C). The addition of complex (5) or (6) greatly simplifies the spectrum. However, with the former the CH<sub>3</sub> and one of the methylene signals are not very clear since these are partially masked by resonances of the complex (Figure 2). Moreover, the downfield shift induced by (6) is more convenient because the resonances of the complex do not interfere. It is important to



**Figure 1.** 100-MHz Proton n.m.r. spectrum of benzyl alcohol (0.2 mol dm<sup>-3</sup>) and [Yb(fod)<sub>3</sub>(pyzy)] (0.2 mol dm<sup>-3</sup>) in CDCl<sub>3</sub>. Chemical shifts in p.p.m. relative to internal SiMe<sub>4</sub>.



**Figure 2.** 60-MHz Proton n.m.r. spectra of dibutyl ether (13 mg, 1.0 × 10<sup>-4</sup> mol) in 0.5 cm<sup>3</sup> CDCl<sub>3</sub> and [Eu(fod)<sub>3</sub>(pyzy)] [(a) 83 mg, 7.4 × 10<sup>-5</sup>; (b) 112 mg, 1.0 × 10<sup>-4</sup> mol]. Chemical shifts in p.p.m. relative to internal SiMe<sub>4</sub>.

mention that the shift in the spectrum of C induced by 112 mg of complex (5) is nearly equal to the shift produced by [Eu(dpm)<sub>3</sub>] {1 × 10<sup>-4</sup> mol of C in 0.5 cm<sup>3</sup> CDCl<sub>3</sub> saturated with [Eu(dpm)<sub>3</sub>]}.<sup>8</sup> The reason for this large shift lies in the fluorocarbon moieties of the fod ligand which increase the solubility of the complex and the residual acidity of the metal cation, making it a better complexing site for weak donors. Thus, it is concluded that even an adduct of [Eu(fod)<sub>3</sub>] can produce better shifts than does [Eu(dpm)<sub>3</sub>], which strengthens the conclusion of Rondeau and Sievers<sup>8</sup> that [Ln(fod)<sub>3</sub>] chelates are the best l.s.r.s. so far studied.

The initial reports on shift reagents<sup>3</sup> employed the bis-(pyridine) adduct of [Eu(dpm)<sub>3</sub>], which was bound to dissociate in order to accommodate an added Lewis base<sup>6</sup> (expanded co-ordination to accommodate an extra ligand and subsequent expulsion of one). In the present experiments the spectra of (CD<sub>3</sub>)<sub>2</sub>SO solutions of the complexes or of the CDCl<sub>3</sub> solutions in presence of added substrates A—C do not exhibit resonances due to free pyrazine or diketone; no change in signal linewidth

or position is seen on keeping the solutions for a few days. This proves that pyrazine as well as the diketone remain co-ordinated in solution even in the presence of added substrate, and there is no dissociation of any of the ligands present.

We have much evidence that in the products the pyrazine is bonded through only one of its nitrogen atoms. This includes the strong band between 950 and 1 000  $\text{cm}^{-1}$  in the i.r. spectra, the n.m.r. spectra which display two resonances for pyrazine in the adducts, no dissociation of the complexes even in the presence of the added base, and inducement of large dipolar shifts in the spectra of A, B, or C. If both nitrogens take part in bonding there would be no free rotation about the Ln-N bond, and an eight-co-ordinate product which will be at least a dimer will be formed. Such complexes are found to be inefficient as l.s.r.s.<sup>3,9,14</sup>

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### References

- 1 D. R. Eaton, *J. Am. Chem. Soc.*, 1965, **87**, 3097; F. A. Hart, J. E. Newbery, and D. Shaw, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3585.
- 2 C. S. Springer, D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, 1967, **6**, 1105.
- 3 C. C. Hinckley, *J. Am. Chem. Soc.*, 1969, **91**, 5160.
- 4 J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 1970, 422.
- 5 J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *Chem. Commun.*, 1970, 749.
- 6 J. Selbin, N. Ahmad, and N. Bhacca, *Inorg. Chem.*, 1971, **10**, 1383.
- 7 N. Ahmad, N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Am. Chem. Soc.*, 1971, **93**, 2564.
- 8 R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, 1971, **93**, 1522.
- 9 N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Am. Chem. Soc.*, 1972, **94**, 8719.
- 10 S. J. Anderson and A. H. Norbury, *J. Chem. Soc., Chem. Commun.*, 1975, 48.
- 11 L. F. Lindoy and H. W. Louie, *Inorg. Chem.*, 1981, **20**, 4186.
- 12 M. Sayeed and N. Ahmad, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3197.
- 13 K. Iftikhar, M. Sayeed, and N. Ahmad, *Indian J. Chem., Sect. A*, 1981, **20**, 1028.
- 14 K. Iftikhar, M. Sayeed, and N. Ahmad, *Inorg. Chem.*, 1982, **21**, 80.
- 15 K. Iftikhar, M. Sayeed, and N. Ahmad, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2258.
- 16 K. Iftikhar and N. Ahmad, *Polyhedron*, 1985, **4**, 333.
- 17 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
- 18 A. B. P. Lever, J. Lewis, and R. S. Nyholm, *Nature (London)*, 1961, **189**, 58; *J. Chem. Soc.*, 1962, 1235, 1963, 5042.
- 19 S. Califano, G. Adembri, and G. Sbrana, *Spectrochim. Acta*, 1964, **20**, 385; R. C. Lord, A. L. Marston, and F. A. Miller, *ibid.*, 1957, **9**, 113; J. D. Simmons, K. K. Innes, and G. M. Begun, *J. Mol. Spectrosc.*, 1964, **14**, 190.
- 20 H. Branick, R. S. T. L. Bruce, H. L. Freeman, N. J. Hair, and J. James, *Inorg. Chem.*, 1976, **15**, 2226.
- 21 H. M. McConnel and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.
- 22 D. R. Crump, J. K. M. Sanders, and D. H. Williams, *Tetrahedron Lett.*, 1970, 4419.
- 23 C. Brecher, H. Samelson, and A. Lempicki, *J. Chem. Phys.*, 1965, **42**, 1081; G. H. Frost, F. A. Hart, C. Health, and M. B. Hursthouse, *Chem. Commun.*, 1969, 1421.

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