

Complexes of some lanthanides with acetoneisonicotinoyl hydrazone: A synthetic and spectral study

GENDA SINGH, MADHU R SRIVASTAVA, PARITI S S J SASTRY
and T R RAO*

Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

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Abstract. Some trivalent lanthanide complexes of acetone isonicotinoylhydrazone (AINH), having the empirical formula $\text{Ln}(\text{AINH})_3\text{Cl}_3$, where $\text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}, \text{Tb(III)}, \text{Dy(III)}$ and Y(III) were prepared. Elemental analyses, molar conductance, magnetic susceptibility, IR, electronic, ^1H , ^{13}C and ^{139}La NMR spectra of the complexes have been examined. It has been found that AINH behaves as a neutral bidentate ligand coordinating through the carbonyl oxygen and azomethine nitrogen. Temperature-dependence of the molar absorptivity and the metal coordination number has been established by the electronic spectra of $\text{Nd}(\text{AINH})_3\text{Cl}_3$ recorded over the 28–80°C range.

Keywords. Lanthanide complexes; Schiff base complexes; isonicotinic acid hydrazide; hepta coordinated Ln complexes.

1. Introduction

The chemistry of lanthanides has assumed considerable importance owing to their increasing use in potentially fluorescent materials and as ideal probes in studies on biological systems (Richardson 1982). Lanthanide ions with their characteristic magnetic and spectral properties are potential probes for the study of natural systems. This is particularly true in the investigation of metal-containing macromolecules in which the metal ion is spectroscopically neutral, e.g., Ca(II) , Mg(II) or Zn(II) . The complexes of amino acids, β -diketones and carboxylic acids of lanthanides show strong fluorescence in which the Eu(III) ion is of special interest because (1) it is used as a spectroscopic probe in bioinorganic chemistry (Bunzli 1987) as well as in ligand conformational analysis (Plancherel 1987), and (ii) it easily substitutes for other metal ions in materials of biological importance. We have, therefore, undertaken a systematic synthetic, magnetic and spectroscopic study of a series of lanthanide complexes and in continuation of our earlier work on Ln(III) complexes of various hydrazides and hydrazones (Rao *et al* 1986, 1989; Rao and Singh 1989, 1990), we report here the results of our investigations on complexes of acetone isonicotinoylhydrazone (AINH) with La(III) , Pr(III) , Nd(III) , Sm(III) , Eu(III) , Gd(III) , Tb(III) , Dy(III) and Y(III) .

* For correspondence

2. Experimental

2.1 Material and methods

Hydrated metal chlorides obtained from Indian Rare Earths Ltd, Kerala, were used as such. Acetone isonicotinoylhydrazone was prepared according to the literature procedure (Fox and Gibas 1953), m.p. 160°C (lit. 161°) Found; C, 61.1; H, 6.23; N, 23.70; N₂H₄, 18.11%. Calcd.; C, 61.01; H, 6.21; N, 23.72; N₂H₄, 18.07%.

2.2 Preparation and analysis of the complexes

Chloro tris(acetone isonicotinoylhydrazone) lanthanide(III) chloride, [Ln(AINH)₃Cl]·Cl₂ and tris(acetone isonicotinoylhydrazone) lanthanide(III) chloride [Ln(AINH)₃]Cl₃ were prepared by mixing together solutions of AINH (6.0 mmol in 20 ml CH₃COCH₃-EtOH mixture) and hydrated lanthanide chloride (2.0 mmol in 20 ml EtOH) and digesting the reaction mixture on a water bath for ~ 1/2 h. The precipitation of the complexes was induced by the addition of 10 ml of CH₃CN. The precipitated complexes were filtered off, washed with EtOH-CH₃CN mixture and dried *in vacuo*.

2.3 Physical measurements

The details of analysis and physical measurements are the same as reported earlier (Rao and Singh 1989). ¹³⁹La NMR spectrum was recorded in DMSO-*d*₆ on a Jeol FX-900 multinuclear NMR spectrometer. The electronic spectra were recorded in 2 × 10⁻² M DMF solutions on a Shimadzu UV-vis spectrophotometer (model-160). The spectral parameters were calculated as reported (Rao and Singh 1989). The mass spectrum was obtained on a Varian Mat CH-7 mass spectrometer at 40°C with a potential of 70 eV. The intensity of the absorption band is measured by the area under the absorption curve and the oscillator strengths (*P*) defined by the expression

$$P = 4.32 \times 10^{-9} [9\eta/(\eta^2 + 2)^2] \int \epsilon(\nu) d\nu,$$

where η is the refractive index of the solvent, ϵ is the molar extinction coefficient and ν is the energy of transition in cm⁻¹ calculated from the reduced expression (Karraker 1967, 1968).

3. Results and discussion

3.1 Characterization of AINH

The IR spectrum of AINH as nujol mull exhibits bands at 1660, 1630 and 1040 cm⁻¹ corresponding to the groups $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{N})$, respectively. the amide I band, however, undergoes a hypsochromic shift to 1690 cm⁻¹ in CH₃CN solution of AINH. The $\Delta(\nu_{\text{CO}})$ which is found to be concentration-dependent, indicates intermolecular H-bonding of the carbonyl group in the solid state and in concentrated solutions of AINH.

The ¹H NMR spectrum of AINH exhibits bands at δ 10.54 and 1.82 due to the

$-\text{NH}-$ and $-\text{CH}_3$ moieties while the signals corresponding to the pyridine ring are observed as two doublets at δ 8.71 and 7.76.

The ^{13}C NMR spectrum of the ligand shows six resonance signals corresponding to nine carbon atoms present in the molecule. The signal at 161.93 ppm is assignable to the carbonyl group. All the other ring-carbon signals and their assignments are, $-\text{C}_2$, 150.22; C_3 , 121.61; C_4 , 141.13 ppm. A careful examination of the ^1H and ^{13}C NMR spectra rules out the existence of AINH in more than one isomeric form under the experimental conditions.

In the mass spectrum of the ligand the base peak at $m/z = 137$ corresponds to $\text{NC}_5\text{H}_4\text{CONHN}^+\text{H}$. The molecular ion peak (M^+) with $m/z = 177$ appears with $\sim 25\%$ relative intensity. The various fragments corresponding to the mass spectral peaks of appreciable intensity are shown in figure 1 (Budzikiewicz *et al* 1964).

The IR, NMR and mass spectral data suggest the structure for AINH as shown in figure 2.

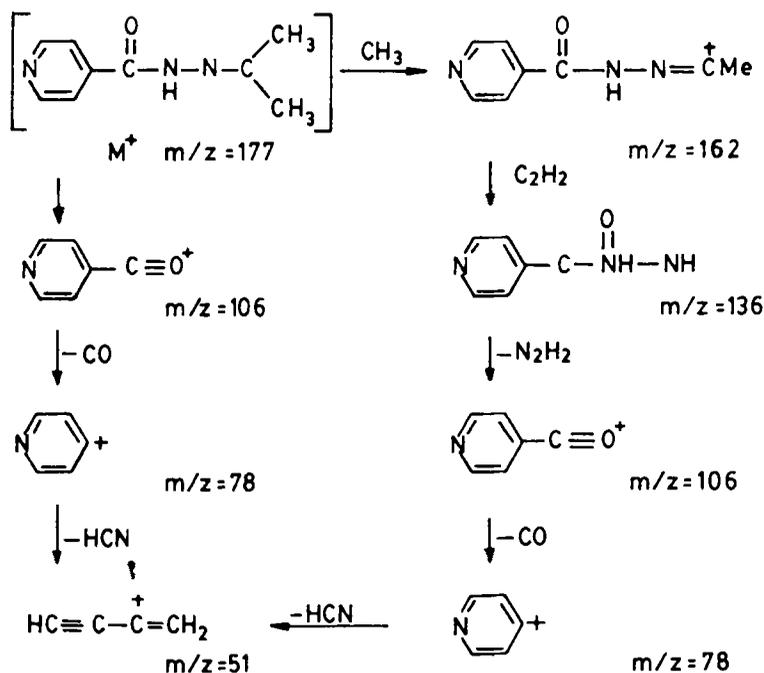


Figure 1. Mass spectral fragmentation path of AINH.

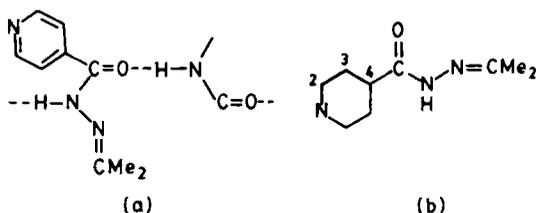


Figure 2. Proposed structure of AINH; (a) solid state with intermolecular H-bonding and (b) Solution in CH_3CN with no H-bonding.

Table 1. Analytical data and general behaviour of Ln(III) complexes of AINH.

Complex	Colour	Decomp. temp. (°C)	Analysis—found (calcd)%				μ_{eff} (B.M.)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
			N	M	Cl	N ₂ H ₄		
[La(AINH) ₃ Cl]Cl ₂	White	212	16.3 (16.2)	18.2 (17.9)	14.0 (13.7)	12.4 (12.4)	diamag.	146.5
[Pr(AINH) ₃ Cl]Cl ₂	Yellow	238	16.2 (16.2)	18.4 (18.1)	13.6 (13.7)	12.4 (12.3)	3.51	138.6
[Nd(AINH) ₃ Cl]Cl ₂	Light blue	278	16.2 (16.1)	18.5 (18.5)	13.5 (13.6)	12.4 (12.3)	4.05	156.7
[Sm(AINH) ₃ Cl]Cl ₂	Light yellow	255	16.1 (16.0)	18.9 (19.1)	13.5 (13.5)	12.4 (12.2)	2.03	152.4
[Eu(AINH) ₃ Cl]Cl ₂	Light yellow	246	16.1 (16.0)	19.1 (19.2)	13.5 (13.5)	12.4 (12.2)	3.36	158.2
[Gd(AINH) ₃]Cl ₃	White	275	15.8 (15.8)	20.1 (19.8)	13.6 (13.4)	12.2 (12.1)	7.31	204.1
[Tb(AINH) ₃]Cl ₃	Cream	286	15.8 (15.8)	20.2 (19.9)	13.4 (13.4)	11.9 (12.1)	8.56	198.6
[Dy(AINH) ₃]Cl ₃	Cream	258	15.9 (15.8)	19.6 (20.3)	13.3 (13.3)	11.8 (12.0)	9.25	212.4
[Y(AINH) ₃]Cl ₃	White	236	17.5 (17.4)	12.1 (12.2)	15.3 (14.7)	13.1 (13.2)	diamag- netic	216.8

3.2 Characterization of the complexes

The analytical data and general behaviour of the complexes (table 1) indicates 1:3 metal to ligand stoichiometry corresponding to the empirical formula Ln(AINH)₃Cl₃. The complexes are moderately hygroscopic and are soluble in water, EtOH, MeOH and coordinating solvents such as DMSO, DMF and pyridine. All the complexes were isolated in reasonably good yields, ranging from 62–88%. The complexes are stable at room temperature but decompose on heating above 212°C. The electrical conductances in 10⁻³ M DMF solution show a 2:1 electrolytic behaviour of the La(III), Pr(III), Nd(III), Sm(III) and Eu(III) complexes and a 3:1 electrolytic nature of the other complexes (Geary 1971).

3.2a Magnetic moments: Room temperature magnetic moments of the complexes corrected for diamagnetism show a slight deviation from Van Vleck values (Van Vleck and Frank 1929) indicating some participation of the 4*f*-electrons in bond formation. The higher value in the case of Sm(III) complex may be due to the temperature-dependent magnetic moment on account of low *J*-separation.

3.2b IR spectra: Bonding sites of AINH involved in complex formation have been determined by a careful comparison of IR spectra of the complexes with that of AINH. To overcome the complications due to the intermolecular hydrogen bonding, the spectra of the complexes have been compared with the solution spectrum of AINH. The bands appearing in the CH₃CN solution spectrum of AINH at 1690, 1630, 1555 and 1295 cm⁻¹ are assigned to amide I, $\nu(\text{C}=\text{N})$, amide II and amide III respectively (Aggarwal and Rao 1978). In the spectra of the complexes the amide I band was

observed at 1660–1655, $\nu(\text{C}=\text{N})$ at 1610–1600, amide II at 1545–1540 and amide III at 1330–1320 cm^{-1} . These observations, consistent with a bathochromic shift of amide I, $\nu(\text{C}=\text{N})$ and amide II and a hypsochromic shift of amide III, suggest bonding through the carbonyl oxygen and azomethine nitrogen (Nagano *et al* 1964; Braibanti *et al* 1968). The observed hypsochromic shift of $\approx 25 \text{ cm}^{-1}$ in the $\nu(\text{N}-\text{N})$ frequency of the complexes also supports coordination through the azomethine nitrogen. The ring-skeletal, in-plane ring-deformation and out-of-plane ring-deformation modes are observed at the same positions as in the ligand, i.e., at 990, 665 and 415 cm^{-1} respectively, thereby suggesting non-coordination of the isonicotinoyl ring nitrogen. All the complexes show medium intensity bands in the 450–340 cm^{-1} region due to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ modes (Nakamoto and Martel 1960) and around 255 cm^{-1} due to $\nu(\text{M}-\text{Cl})$ (Nakamoto 1986).

3.2.3 Electronic spectra

The electronic spectral transitions and their oscillator strengths are given in table 2. The complexes showed an increase in oscillator strengths (Carnal *et al* 1968; Itikhar 1987) in comparison to the corresponding aqua-ion except for the transition, $^3\text{H}_4 \rightarrow ^4\text{P}_2'$ of the Pr(III) complex which records a decrease. An enormous (three-fold) increase observed in the oscillator strength (P) of the hypersensitive transition in $\text{Nd}(\text{AINH})_3\text{Cl}_3$ suggests a lower molecular symmetry (Karraker 1967, 1971).

An attempt has been made to correlate metal coordination number and shape of the hypersensitive band. The nujol mull and DMF solution spectra of the Nd(III) complex show almost similar profiles with sharper features in the latter. It may, therefore, be inferred that there is no change in coordination due to solvation effects, as is the case for instance with the β -diketonate complexes of neodymium (Karraker 1968). The profile of the above band closely resembles that of the seven coordinated $\text{Nd}(\text{thd})_3 \cdot \text{HFAA}$ in CHCl_3 (Karraker 1968) ($\text{thd} = (\text{CH}_3)_3\text{CCOCHCOC}(\text{CH}_3)_3$; $\text{HFAA} = \text{CF}_3\text{COCHCOCF}_3$). The effect of the environment on the hypersensitive transition was examined by measuring the spectra over a range of temperatures (30–80°C) (figure 3) in the 550–650 nm spectral region. There was a remarkable decrease in the absorption of the hypersensitive band as the temperature increased (Krumholtz 1958). Such behaviour is known to support the presence of dynamic coupling due to a structure which is devoid of inversion of symmetry (Henrie *et al* 1976). Further, the hypersensitive band shows a peculiar change in its spectral profile with increasing temperature and the pattern at 80°C clearly corresponds to a change in coordination number from seven to six. The higher temperature spectral profile clearly resembles that of the six-coordinated $\text{Nd}(\text{DPPD})_3$ ($\text{DPPD} = \text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5$) (Karraker 1968). The decrease in coordination number at higher temperature may presumably be due to the shift of a chloride ion to the outside of the coordination sphere. Various spectral parameters, viz., nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), covalency ($\delta\%$) and angular overlap parameter (η) have been calculated as earlier (Rao and Singh 1989a). All these parameters suggest weak covalent nature of the metal–ligand bond.

3.2.4 ^1H and ^{13}C NMR spectra

^1H and ^{13}C NMR spectra of AINH and the La(III) and Y(III) complexes were recorded in $\text{DMSO}-d_6$. The $-\text{NH}-$ resonance signals appearing at δ 10.91(s) and δ

Table 2. Electronic spectral data* and oscillator strengths of Ln(III) complexes of AINH.

Complex	Band maxima (cm ⁻¹)		Assignments	Oscillator strength $P \times 10^6$	Spectral parameters
	Nujol	DMSO			
[Pr(AINH) ₃ Cl]Cl ₂	16,365-17,330	16,360-17,280	³ H ₄ → ¹ D ₂	8.36	$\bar{\beta} = 0.9661$
	20,200-20,445	20,190-20,750	→ ³ P ₀	6.89	$b^{1/2} = 0.1302$
	20,745-21,410	20,750-21,415	→ ³ P ₁	2.86	$\eta = 0.0174$
	21,415-22,725	21,420-22,690	→ ³ P ₂	3.45	$\delta\% = 3.5083$
	11,175-11,695	11,040-11,665	⁴ I _{9/2} → ⁴ F _{3/2}	4.54	$\bar{\beta} = 0.9926$
[Nd(AINH) ₃ Cl]Cl ₂	11,975-12,820	12,020-12,690	→ ⁴ F _{5/2}	7.02	$b^{1/2} = 0.0615$
	12,935-13,795	13,020-13,660	→ ⁴ F _{7/2} , ⁴ S _{3/2}	6.46	$\eta = 0.0038$
	14,325-14,925	14,305-14,795	→ ⁴ F _{9/2}	1.48	$\delta\% = 0.7463$
	16,395-17,480	16,475-17,535	→ ⁴ G _{5/2} , ² G _{7/2}	29.26	
	18,520-19,610	18,585-19,800	→ ⁴ G _{7/2} , ⁴ G _{9/2}	5.46	
	20,704-21,850	—	→ ² D _{3/2}	—	
	20,410-21,365	—	⁶ H _{5/2} → ⁴ I _{9/2}	—	$\bar{\beta} = 0.9973$
	21,365-21,980	21,365-21,970	→ ⁴ I _{11/2}	—	$b^{1/2} = 0.0371$
[Eu(AINH) ₃ Cl]Cl ₂	21,360-21,565	21,365-21,645	⁷ F ₀ → ³ D ₂	—	$\eta = 0.0014$
	25,140-25,580	25,190-25,640	→ ⁵ L ₆	—	$\delta\% = 0.2705$
					$\bar{\beta} = 0.9998$
					$b^{1/2} = 0.0105$
					$\eta = 0.0001$
					$\delta\% = 0.0201$

* Spectral parameters calculated from nujol mull spectra.

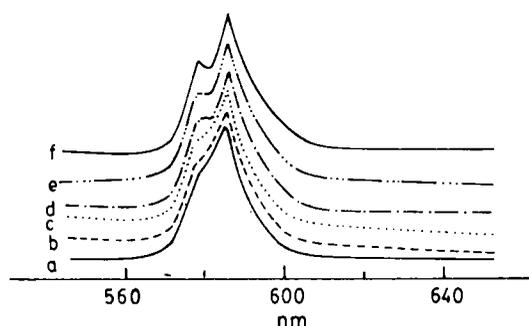


Figure 3.

10.86(s) in the La(III) and Y(III) complexes respectively, indicate a downfield shift w.r.t. AINH (δ 10.48) coupled with broadening. The above data suggest coordination of the carbonyl/azomethine moiety (Patil and Kulkarni 1982; Rao and Singh 1990) of the ligand. A further support for coordination through the azomethine moiety has been inferred from the downfield shift of the $-\text{CH}_3$ signal (from δ 1.82 to \sim 2.00(d)). The coupling constants of the pyridine ring doublets (C_2H and C_3H with $\delta = 4.25$ Hz) are almost the same in the complexed and uncomplexed AINH (at δ 8.69(d) for δ - C_2H and δ 7.75(d) for $-\text{C}_3\text{H}$) thereby, ruling out the participation of the isonicotinoyl ring nitrogen in coordination.

In the ^{13}C NMR spectra, the numbering scheme of the carbon atoms is as shown in figure 2. The assignments for the ligand have been deduced taking into account the shifts of the carbon atoms of the fragments which form the AINH molecule (Rao and Singh 1989b, 1990). The carbonyl group coordination was inferred from the significant downfield shift of the >C=O resonance signal in the complexes (AINH, 161.93 ppm; La(III) complex, 164.83 ppm and Y(III) complex, 164.18 ppm) (Paolucci *et al* 1980; Domiano *et al* 1984). Besides, the downfield shift of the $-\text{CH}_3$ signals (from 24.98 and 18.16 ppm to 25.20 and 18.60 ppm) suggests coordination through the azomethine nitrogen. The ring carbon signals, however, remained unaltered except for the C_4 signal which shows an upfield shift, (141.13 to 139.69 ppm) inferring non-coordination of the ring nitrogen. The upfield shift of the above signal may be due to an increase in the electron density through conjugation consequent to the coordination through the paracarbonyl group.

^{139}Ln NMR spectrum consists of a broad resonance signal resulting from quadrupole relaxation owing to the moderate quadrupole moment (Q) ($0.21 \times 10^{-24} \text{ cm}^2$). The ^{139}La chemical shift was measured relative to the most dilute pure aqueous $\text{La}(\text{ClO}_4)_3$ solution, used as an external reference. The resonance signal of the complex was observed as a single line at -189.0 ppm with a width at half-height ($W_{1/2}$), 5130 Hz. The large value of $W_{1/2}$ indicates the unsymmetrical nature of the complex (Evans and Missen 1982) or a reduction in the symmetry of the local electronic environment of the ion (Fratiello *et al* 1989). The reported range of ^{139}La chemical shifts is quite large and the shifts are roughly correlated with the extent of covalency in the La-ligand bonds, with greater covalency bonding to deshielding (Evans and Missen 1982). However, all the ligands which coordinate through oxygen seem to give complexes in which the chemical shifts lie in a fairly narrow region around zero while for N-donor ligands there exists a monotonic relationship between δ and the number of ligand

N-atoms coordinated (Evans and Missen 1982). The chemical shift (-189.0 ppm) observed in the present case is consistent with weak covalency in the metal–ligand bond.

4. Conclusion

The analytical data and general behaviour of the complexes suggest the empirical formula $\text{Ln}(\text{AINH})_3\text{Cl}_3$. The electrical conductance suggests a 2:1 electrolytic nature of the complexes with the exception of Gd(III), Tb(III), Dy(III) and Y(III) which show 3:1 electrolytic behaviour. The IR, ^1H and ^{13}C NMR spectra suggest neutral bidentate behaviour of the AINH coordinating through the carbonyl oxygen and the azomethine nitrogen. The absorption spectrum show the feeble covalent nature of the metal AINH bond. Temperature variation had a profound effect on the absorption of hypersensitive band as well as the coordination number of the neodymium complex. A seven-coordination around La(III)–Eu(III) and a six-coordination around Gd(III)–Dy(III) and Y(III) have been inferred in the present complexes.

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References

- Aggarwal R C and Rao T R 1978 *J Inorg. Nucl. Chem.* **40** 171
Braibanti A, Dallavalle F, Pellinghelli M A and Laporati G 1968 *Inorg. Chem.* **7** 1430
Budzickiewicz H, Djerossi C and William D H 1964 *Structure elucidation of natural products by mass spectrometry* (San Francisco: Holdenday) p. 189
Bunzli J C G 1981 *Inorg. Chim. Acta* **139** 219
Carnal W T, Fields P R and Rajnak K 1968 *J. Chem. Phys.* **49** 4412
Domiano P, Pelizzi C, Predieri G, Viglani C and Palla G 1984 *Polyhedron* **3** 281
Evans D F and Missen P H 1929 *J. Chem. Soc., Dalton Trans.* 1982
Fox H H and Gibas J T 1953 *J. Org. Chem.* **18** 983
Fratiello A, Anderson V K, Bolinger A, Cordero C, De Merit B, Flores T and Perrigan R D 1989 *J. Sol. Chem.* **18** 313
Geary W J 1971 *Coord. Chem. Rev.* **7** 81
Henrie D E, Fellows R L and Choppin G R 1976 *Coord. Chem. Rev.* **18** 199, and references therein
Ifikhar K 1987 *Inorg. Chim. Acta* **129** 261
Karraker D G 1967 *Inorg. Chem.* **6** 1863
Karraker D G 1968 *Inorg. Chem.* **7** 473
Karraker D G 1971 *J. Inorg. Nucl. Chem.* **33** 3713
Kurmholz P 1958 *Spectrochim. Acta* **10** 274
Nagano K, Kinoshita H and Hirakawa A 1964 *Chem. Pharm. Bull.* **12** 1198
Nakamoto K 1986 *Infrared and Raman spectra of inorganic and coordination compounds* 4th edn (New York: John Wiley) p. 206
Nakamoto K and Martel A E 1960 *J. Chem. Phys.* **32** 588
Paolucci G, Marangoni G, Bandoli G and Clemente D A 1980 *J. Chem. Soc., Dalton Trans.* p. 1304
Patil S A and Kulkarni V H 1984 *Inorg. Chim. Acta* **95** 195

- Plancherel D 1987 *Inorg. Chem. Acta* **139** 297
Rao T R, Khan I A and Aggarwal R C 1986 *J. Less Common Met.* **115** 325
Rao T R and Singh G 1989a *Trans. Met. Chem.* **14** 471
Rao T R and Singh G 1989b *Synth. React. Inorg. Met.-Org. Chem.* **19** 263
Rao T R and Singh G 1990a *Synth. React. Inorg. Met.-Org. Chem.* **20** 377
Rao T R and Singh G 1990b *Indian J. Chem.* **29A** 154, 716
Rao T R, Singh G and Khan I A 1989 *Trans. Met. Chem.* **14** 15
Richardson F S 1982 *Chem. Rev.* **82** 541
Van Vleck J H and Frank A 1929 *Phys. Rev.* **34** 1494