Reactions of $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$; L_2 = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2PPh_2$) with 1,4-Piperazinedicarbonitrile or 1-Piperidinecarbonitrile in the Presence of an Anion (BF_4^-, PF_6^-, BPh_4^-, or ClO_4^-)

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Reactions of $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$; L_2 = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2PPh_2$) have been carried out with 1-piperidinecarbonitrile or 1,4-piperazinedicarbonitrile in the presence of a suitable anion (PF_6^-, BF_4^-, BPh_4^-, or ClO_4^-). The products were found to be cationic mono- and bi-nuclear complexes which have been characterised by elemental analyses and spectroscopic (i.r., u.v.–visible, and n.m.r.) studies. Conductivity measurements have also been carried out to confirm the charges on these cationic species.

A number of structures containing cyanamide (NH_2CN) having the two nitrogen atoms situated in significantly different electronic environments and thus making their nucleophilicity different have been proposed.[1–15] No definite structural decision regarding the nature of the orbital (sp^3 or p_z) containing the lone pair of electrons on the amino nitrogen has yet been arrived at conclusively.[1–15] Although a variety of synthetic organic reactions involving cyanamide and carbodi-imide nitrogen as a nucleophile have been reported,[16–18] very little work has been carried out so far with regard to electrophilic attack of metal ions/complexes on the terminal electron-rich nitrogens. There is a likelihood of many of these reactions being nitrogen nucleophilicity dependent. In addition, the presence of a tautomeric equilibrium between the amide (major) and di-imide (minor) forms of cyanamide might complicate the reaction products.[3–8,19,20]

Over the past few years we have been interested in studying the nucleophilic character of the nitrogen of metal-bonded cyano groups and wished to exploit this nucleophilicity in synthesising bridged metal complexes;[21–24] thus a study of the interaction of $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$; L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Ph_2PCH_2PPh_2$ (dppm)] with 1,4-piperazinedicarbonitrile or 1-piperidinecarbonitrile has been undertaken. The carbonitrile ligands exist only in the nitrile form and unlike cyanamide a tautomeric equilibrium will not complicate the reaction path. This paper reports the products of the reactions which have been characterised by elemental analyses, spectroscopic (i.r., u.v.–visible, and n.m.r.) studies, and conductivity measurements.

Experimental

All chemicals were AnalaR grade and used without further purification. Solvents were dried before use.[25] The complexes $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$; L_2 = dppe or dppm) were prepared by the literature methods.[26–29] Analytical and spectral data of the products were obtained as described elsewhere.[27] The electronic spectra (200—700 nm) of the complexes in chloroform solution were recorded on a Shimadzu U.V. 190 spectrophotometer. The ^{13}C n.m.r. spectra were obtained on a JEOL FT-90 spectrophotometer. Conductivity measurements were carried out in dry methanol using an Elico conductivity bridge type CM82T.

Reaction of 1,4-*Piperazinedicarbonitrile with* $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (L = PPh_3, $AsPh_3$, *or* $SbPh_3$; L_2 = dppe *or* dppm) *in the presence of a Suitable Anion.*—A typical reaction procedure was as follows. The complex $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (0.13 mmol) was suspended in dry methanol (25 cm^3) containing a salt of a suitable anion (NH_4PF_6, $NaBF_4$, $NaBPh_4$, or $LiClO_4$) (0.25 mmol) and 1,4-piperazinedicarbonitrile (0.14 mmol). The contents of the flask were refluxed for *ca.* 1 h whereby $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ started to dissolve slowly and bright yellow shining crystals of a complex appeared. These were separated by centrifugation. Further crystals were obtained by slow concentration of the centrifugate on a water-bath. The crystals were washed with methanol, diethyl ether, and light petroleum and dried under vacuum (yield, *ca.* 58%). Analyses corresponded to the formula $[Ru_2(\eta^5\text{-}C_5H_5)_2(L_2)_2(\mu\text{-}C_6H_8N_4)]X_2$ (L = PPh_3, $AsPh_3$, or $SbPh_3$; L_2 = dppe or dppm; X = PF_6, BF_4, BPh_4, or ClO_4).

Reaction of 1-*Piperidinecarbonitrile with* $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (L = PPh_3, $AsPh_3$, *or* $SbPh_3$; L_2 = dppe *or* dppm) *in the Presence of a Suitable Anion.*—A typical reaction procedure was as follows. A suspension of $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (0.13 mmol), a salt of a suitable anion (NH_4PF_6, $NaBF_4$, $NaBPh_4$, or $LiClO_4$) (0.25 mmol), and 1-piperidinecarbonitrile (0.18 mmol) was taken in dry methanol (25 cm^3). The resulting suspension was heated to reflux for *ca.* 2—3 h, whereupon the suspension dissolved to give a bright yellow solution. The resulting solution was concentrated slowly on a water-bath to nearly 5 cm^3 whereby yellow crystals separated out. These were separated by centrifugation, washed with methanol, diethyl ether, and light petroleum and dried under vacuum (yield, *ca.* 50%). Analyses corresponded to the formula $[Ru(\eta^5\text{-}C_5H_5)L_2(C_6H_{10}N_2)]X$ (L = PPh_3, $AsPh_3$, or $SbPh_3$; L_2 = dppe or dppm; X = PF_6, BF_4, BPh_4, or ClO_4).

Results and Discussion

Reactions of $[Ru(\eta^5\text{-}C_5H_5)ClL_2]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$; L_2 = dppe or dppm) with 1,4-piperazinedicarbonitrile or 1-piperidinecarbonitrile in the presence of a suitable anion (PF_6^-, BF_4^-, BPh_4^-, or ClO_4^-) yielded bright yellow cationic binuclear and mononuclear complexes respectively. Microanalytical data suggested the formulae given in the Table. They are non-hygroscopic, slightly soluble in methanol, chloroform,

Table. Analytical and physical data[a]

Ligands L or L_2				M.p.[b]/°C	Anion X^-	Analysis (%) Found (calc.)			U.v. spectra $\lambda_{max.}$/nm (log ε)
						C	H	N	
P	P	P	P	165—170	BF_4	61.8 (62.4)	4.65 (4.60)	3.50 (3.30)	
P	P	P	P	179	PF_6	58.1 (58.4)	4.35 (4.30)	2.90 (3.10)	358 (4.68)
P	P	P	P	165	BPh_4	74.9 (75.7)	5.20 (5.40)	2.40 (2.60)	
P	P	P	P	167	ClO_4	—	—	—	
A	P	A	P	175	BF_4	58.8 (59.3)	4.50 (4.40)	2.90 (3.10)	
A	P	A	P	175—180	PF_6	56.5 (55.7)	4.25 (4.10)	2.55 (2.95)	361.5 (4.72)
A	P	A	P	157—160	BPh_4	72.65 (72.70)	6.00 (5.30)	2.80 (2.50)	
A	P	A	P	169—171	ClO_4	—	—	—	
A	A	A	A	179	BF_4	55.4 (56.6)	4.05 (4.20)	2.40 (3.00)	
A	A	A	A	182	PF_6	54.05 (53.30)	4.30 (3.90)	2.85 (2.80)	360 (4.71)
A	A	A	A	162—164	BPh_4	69.5 (70.0)	5.50 (5.05)	2.30 (2.40)	
A	A	A	A	175	ClO_4	—	—	—	
Sb	Sb	Sb	Sb	174	BF_4	52.20 (51.40)	4.85 (3.80)	2.15 (2.70)	
Sb	Sb	Sb	Sb	193—195	PF_6	49.7 (48.6)	4.75 (3.60)	2.85 (2.60)	365 (4.76)
Sb	Sb	Sb	Sb	161	BPh_4	65.2 (64.8)	4.60 (5.00)	2.60 (2.35)	
Sb	Sb	Sb	Sb	165	ClO_4	—	—	—	
dppe		dppe		248	BF_4	56.20 (56.75)	4.85 (4.60)	3.60 (3.90)	
dppe		dppe		252	PF_6	51.65 (52.40)	5.10 (5.20)	3.90 (3.50)	363.5 (4.52)
dppe		dppe		239	BPh_4	72.80 (73.20)	4.40 (5.55)	2.85 (2.95)	
dppe		dppe		240	ClO_4	—	—	—	
dppm		dppm		158	BF_4	55.80 (56.15)	4.50 (4.40)	3.40 (3.95)	
dppm		dppm		162—164	PF_6	50.65 (51.60)	4.20 (4.05)	3.15 (3.60)	362.5 (4.45)
dppm		dppm		160	BPh_4	73.4 (72.9)	5.90 (5.40)	2.75 (3.00)	
dppm		dppm		164	ClO_4	—	—	—	
P		P		168	BF_4	62.90 (63.60)	5.30 (5.05)	3.00 (3.15)	
P		P		170—172	PF_6	60.70 (59.70)	4.95 (4.75)	2.90 (3.00)	350 (3.40)
A		P		162	BF_4	61.10 (60.60)	4.30 (4.85)	2.65 (3.00)	
A		P		167	PF_6	57.60 (57.00)	5.00 (4.55)	2.30 (2.85)	
A		A		159	BF_4	58.20 (57.85)	4.45 (4.60)	2.60 (2.85)	
A		A		162—165	PF_6	55.20 (54.60)	5.00 (4.35)	2.65 (2.70)	352 (3.23)
Sb		Sb		173	BF_4	52.05 (52.75)	4.70 (4.20)	2.50 (2.60)	
Sb		Sb		179	PF_6	49.80 (50.05)	3.70 (4.00)	2.15 (2.50)	
	dppe			240	BF_4	57.9 (58.3)	5.40 (5.10)	3.70 (3.65)	
	dppe			246	PF_6	53.8 (54.2)	4.30 (4.75)	3.10 (3.40)	360.2 (3.51)
	dppm			162	BF_4	58.2 (57.8)	4.75 (4.90)	3.20 (3.75)	
	dppm			172—174	PF_6	54.0 (53.6)	4.80 (4.45)	3.25 (3.45)	358 (3.62)

[a] P = PPh_3, A = $AsPh_3$, Sb = $SbPh_3$, dppe = 1,2-bis(diphenylphosphino)ethane, and dppm = bis(diphenylphosphino)methane. [b] All complexes were yellow.

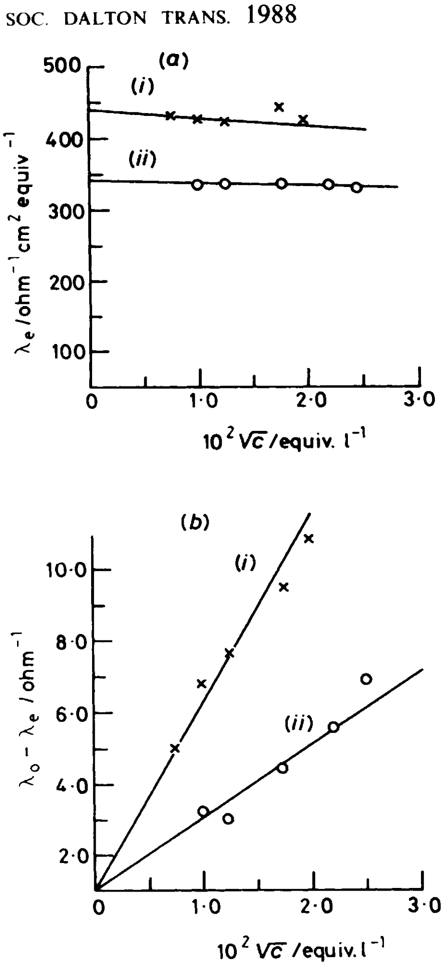


Figure 1. Plots of (*a*) equivalent conductance λ_e *vs.* $\sqrt{c}$ and (*b*) $(\lambda_0 - \lambda_e)$ *vs.* $\sqrt{c}$ for (*i*) $[Ru_2(\eta^5\text{-}C_5H_5)_2(PPh_3)_4(\mu\text{-}C_6H_8N_4)][PF_6]_2$ and (*ii*) $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(C_6H_{10}N_2)]PF_6$

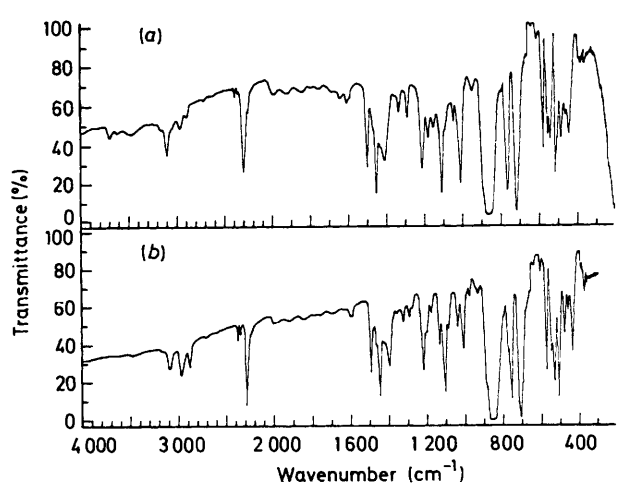


Figure 2. Infrared spectra of (*a*) $[Ru_2(\eta^5\text{-}C_5H_5)_2(PPh_3)_4(\mu\text{-}C_6H_8N_4)][PF_6]_2$ and (*b*) $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(C_6H_{10}N_2)]PF_6$

dichloromethane, acetone, benzene, and other halogenated organic solvents and insoluble in light petroleum or diethyl ether.

The distinction between the charges on the cationic species has also been confirmed by their conductivity measurements in highly pure and dry methanol, according to a procedure adopted by Feltham and Hayter.[30] They emphasized the need to carry out conductance measurements over a concentration range in order to distinguish between mononuclear and polynuclear species. From the values of the equivalent conductance (λ_e) in the concentration range $10^{-2} - 10^{-4}$ equiv. l^{-1}, the equivalent conductance at zero concentration (λ_0) was determined by extrapolation (Figure 1) and subsequently values of $\lambda_0 - \lambda_e$ [Figure 1(*b*)] were plotted as a function of $\sqrt{c}$.[31–33] The slopes of these straight lines for the 1-piperidinecarbonitrile (271) and 1,4-piperazinedicarbonitrile (607) complexes compared very well with Feltham's values for 1:1 and 1:2 complexes, 288 and 552 respectively,[34,35] providing further evidence regarding the charges on the cations. The bonding modes in the complexes and their tentative structures have been deduced following spectral studies.

I.r. Spectra.—The model considered for the interpretation of the i.r. spectra of the complexes is assumed to be a *N,N*-disubstituted nitrile ($>N\text{–}C{\equiv}N$). The possibility of the ligands existing in the carbodi-imide form ($-N{=}C{=}N-$) does not exist except for the contribution of a resonating structure where the lone pair on the $>$ N–nitrogen participates in a delocalisation process with separation of the charges ($>N^+{=}C{=}N^-$).[1–3] This will have some contribution only when the lone pair is present in the pure p_z orbital. According to the $>N\text{–}C{\equiv}N$ model, the i.r. spectra of 1-piperidinecarbonitrile, with C_s symmetry, should exhibit i.r.-active bands due to ν(C≡N), ν(C–N), and δ(NCN) around 2 200, 1 000, and 400 cm^{-1} respectively.[1] Presuming the carbodi-imide model the vibrational spectra should differ because of the difference in the position of ν_{sym}(N=C=N) and two NCN bending modes. The values of the fundamental mode frequencies and the force constants of ν(N–C≡N) and ν(N=C=N) should undoubtedly be similar, but if the two CN modes of ν(N=C=N) are equivalent, a slightly lower value of ν_{asym}(N–CN) (2 070 cm^{-1}) than that of ν(C=N) may be expected and the intensity of the symmetric stretching mode in N=C=N should be much smaller.[1,36] In the spectrum of 1-piperidinecarbonitrile two intense bands were found at 2 240 and 1 010 cm^{-1} and a weak broad band, at 430 cm^{-1}, attributable to ν(C≡N), ν(C–N), and δ(NCN) respectively; the ν(C–N) band at 1 010 cm^{-1} is single and very sharp suggesting it to be unaffected by the 'neighbour interaction'.[2] In addition, there is a distinct splitting of ν(C≡N) (not present in the spectra of the complexes), which may be because of the Fermi resonance between ν(C≡N) and the overtone frequency involving the ν(C–N) stretch. It is also likely that the non-involvement of the lone pair in resonance structures of $>N\text{–}C{\equiv}N$ may be related to the molecular non-polarity[3] because of which the non-bonding orbital located at $>N-$ of the $>N\text{–}C{\equiv}N$ moiety instead of being in a pure p_z orbital, also has some *s* character and thus inhibits the contribution of $>N^+{=}C{=}N^-$ to the structure.

The i.r. spectra of the complexes of 1-piperidinecarbonitrile show bands at 2 285 (single), 1 010, and 430 cm^{-1} respectively. The shift of the band at 2 240 cm^{-1} to 2 285 cm^{-1} implies direct co-ordination of ruthenium to the nitrogen of the C≡N group. Furthermore the shift also indicates the absence of π-back-bonding from ruthenium and co-ordination through the triple bond of the CN group, which would cause a shift towards lower wavenumbers. The position of ν(C–N) at 1 010 cm^{-1} remained the same suggesting no effect on the $>$N–C bond order by co-ordination and implying non-involvement of the amide nitrogen lone pair in metal co-ordination. The i.r. spectra of 1,4-piperazinedicarbonitrile and its complexes are, as expected similar to those of 1-piperidinecarbonitrile and its complexes (Figure 2). The two $>N\text{–}C{\equiv}N$ groups, being too far separated, do not interact to cause either broadening or splitting of the

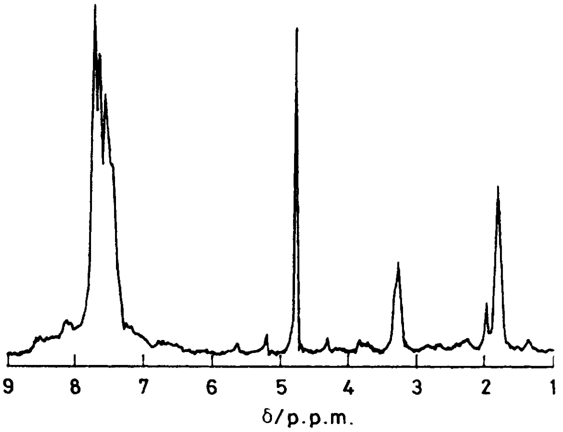


Figure 3. ^1H n.m.r. spectrum of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(C_6H_{10}N_2)]PF_6$

ν(N–C≡N) bands. Unfortunately we are unable to assign conclusively ν(Ru–N) because of the presence of a number of bands in the lower wavenumber region. Nonetheless a band at 430 cm^{-1} has tentatively been assigned to ν(Ru–N). This band does not exist in the free ligand spectra.

Electronic Spectra.—The electronic spectra of the mono- and bi-nuclear complexes show a broad medium intensity band centred around 360 nm (Table) which we assign to a metal to ligand charge-transfer (m.l.c.t.) transition (Ru^{II} to the antibonding C_5H_5 orbitals). The possibility of this band arising from other m.l.c.t. transitions may be ruled out since the likelihood of transitions appearing from Ru^{II} to either EPh_3 or the antibonding C≡N orbitals in the near u.v. region (λ = 350 nm) is obscure[37] The band at 360 nm did not show any solvatochromic effect indicating no change in the dipole moments of the molecule in the ground and excited states; this further supports our assignment because the presence of a ruthenium to 1-piperidinecarbonitrile or 1,4-piperazinedicarbonitrile charge-transfer band would change the dipole moment of the excited states.

Bands present in the 200—330 nm region were impossible to assign due to the extensive overlapping of a number of intraligand and other m.l.c.t. bands.[37] The complexes did not exhibit any bands in the visible region.

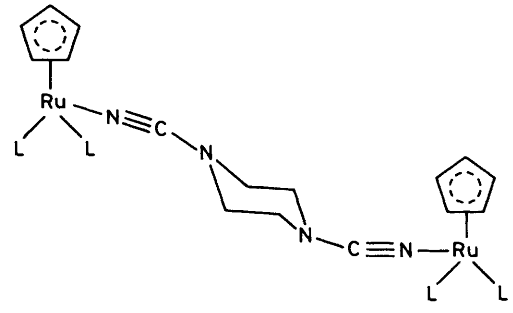
N.M.R. Spectra.—^1H N.m.r. spectra of the 1,4-piperazinedicarbonitrile complexes exhibited peaks around δ 7.2—7.5 (EPh_3), 4.65 ($\eta^5\text{-}C_5H_5$), and 3.1 (CH_2 protons of the piperazine ring). In the spectra of the 1-piperidinecarbonitrile complexes peaks appeared around δ 7.4—7.7 (EPh_3, E = P, As, or Sb), 4.7 ($\eta^5\text{-}C_5H_5$), and 3.25, 1.95, and 1.8 (CH_2 protons of piperidine ring) (Figure 3).

The positions of the C_5H_5 protons in the spectra of both complexes were comparable with those of $[Ru(\eta^5\text{-}C_5H_5)(EPh_3)(CN)]$ (E = P, As, or Sb).[38] This suggests that the >N–C≡N moiety affects the environment around the C_5H_5 protons in a similar manner to the C≡N group. The nitrogen atom attached to –C≡N in the >N–C≡N moiety does not seem to have much effect on the C_5H_5 protons through their lone pair. This further supports the non-involvement of the nitrogen lone pair in the resonance possibly due to the molecular non-planarity (*cf.* i.r. spectra).

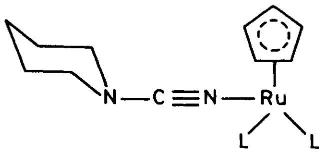
^{13}C N.m.r. spectra of the complexes showed that the carbon of >N–C≡N resonates at around δ 137.7—138.7 p.p.m. and exhibits a distinct shift towards a lower field compared to that in 1-piperidinecarbonitrile or 1,4-piperazinedicarbonitrile (δ 117 p.p.m.). This indicates deshielding of the carbon atom in the >N–C≡N moiety on co-ordination. It could be that on complexation of nitrogen to ruthenium, the electron density on the carbon atom of the –C≡N group is polarized towards nitrogen resulting in deshielding of the carbon nucleus. It is also noteworthy that if the amide nitrogen lone pair was involved in the resonance, the possibility of deshielding should have been much less, thus again supporting the non-planarity of the molecule.

Based on the above spectral, analytical, and conductivity data, it appears certain that the metal is co-ordinated through the nitrogen of the CN group, however the molecules may have a number of conformers (chair, boat, *cis–trans etc.*).

The existence of the complexes of 1,4-piperazinedicarbonitrile in the boat form could be tentatively ruled out on the following grounds. (*i*) The steric interaction between the two NCN groups present in 1,4 positions will be very prominent making the boat form highly unstable and energetically unfavourable. (*ii*) Lone pair–lone pair repulsions on the two nitrogen atoms of the ring should make the boat form energetically less favourable compared to the chair form. Thus the chair form is preferred (see below) in which the nitrogens of the piperazine ring are far apart and the substituents in *trans* positions.



Similarly in the 1-piperidinecarbonitrile complexes the chair form is also preferred with the NCN substituent occupying an equatorial position to avoid steric interaction with the neighbouring CH_2 groups within the ring (see below).



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References

1 G. D. Wagner, jun., and E. L. Wagner, *J. Phys. Chem.*, 1960, **64**, 1480.
2 S. T. King and J. H. Strope, *J. Chem. Phys.*, 1971, **54**, 1289.
3 W. H. Fletcher and F. B. Brown, *J. Chem. Phys.*, 1963, **39**, 2478.
4 L. Kahovec and K. W. F. Kohlrausch, *Z. Phys. Chem. (Leipzig)*, 1937, **B37**, 421; 1944, **193**, 188.
5 W. C. Schneider, *J. Am. Chem. Soc.*, 1950, **72**, 761.
6 J. Ploquin and C. Vergneac-Souvray, *Compt. Rend.*, 1952, **97**, 234.
7 W. G. Moulton and R. A. Kromhout, *J. Chem. Phys.*, 1956, **25**, 34.
8 L. Hunter and H. A. Rees, *J. Chem. Soc.*, 1945, 617.
9 M. Davies and W. J. Jones, *Trans. Faraday Soc.*, 1958, **54**, 1454.
10 G. P. Shipulo, *Opt. Spectrosc.*, 1961, **10**, 288.
11 D. R. Lide, jun., *J. Mol. Spectrosc.*, 1962, **8**, 142.

12 D. J. Millen, G. Topping, and D. R. Lide, jun., *J. Mol. Spectrosc.*, 1962, 153.

13 Table 1 in, J. N. Macdonald, D. Taylor, J. K. Tyler, and J. Sheridan, *J. Mol. Spectrosc.*, 1968, **26**, 285.

14 J. B. Moffat and C. Vogt, *J. Mol. Spectrosc.*, 1970, **33**, 494.

15 J. R. Durig, M. Walker, and F. G. Boglin, *J. Chem. Phys.*, 1968, **48**, 4675.

16 H. G. Khorana, *Chem. Rev.*, 1953, **53**, 145 and refs. therein.

17 F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, 1967, **67**, 107 and refs. therein.

18 A. Williams and I. T. Ibrahimo, *Chem. Rev.*, 1981, **81**, 589 and refs. therein.

19 Y. Otagiri, *Nippon Kagaku Zasshi*, 1949, **70**, 263.

20 S. Imanishi and T. Tachi, *Nippon Kagaku Zasshi*, 1942, **63**, 492.

21 P. Rigo and A. Turco, *Coord. Chem. Rev.*, 1974, **13**, 133.

22 P. L. Gaus and A. I. Crumbliss, *Inorg. Chem.*, 1976, **15**, 2080.

23 I. A. Davis, F. R. Hartley, S. G. Murray, and M. A. Pieru-Butler, *J. Chem. Soc., Dalton Trans.*, 1983, 1305.

24 G. J. Baird, S. G. Davis, S. D. Moon, S. I. Simpson, and R. H. Jones, *J. Chem. Soc., Dalton Trans.*, 1985, 1479.

25 A. I. Vogel, 'A Text book of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1951.

26 M. I. Bruce and N. J. Windsor, *Aust. J. Chem.*, 1977, **30**, 1601.

27 K. M. Rao, L. Mishra, and U. C. Agarwala, *Polyhedron.*, 1986, **5**, 791.

28 K. M. Rao, L. Mishra, and U. C. Agarwala, *Indian J. Chem., Sect. A*, 1987, **27**, 755.

29 G. S. Ashby, M. I. Bruce, I. B. Tomkins, and R. C. Wallis, *Aust. J. Chem.*, 1979, **32**, 1003.

30 R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

31 R. G. Hayter, *J. Am. Chem. Soc.*, 1962, **84**, 3046; R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, 1963, **2**, 306.

32 R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 1038.

33 J. Chatt and R. C. Hayter, *J. Chem. Soc.*, 1961, 896.

34 A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, 1967, **6**, 458.

35 F. A. Catton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, 1967, **6**, 931.

36 M. A. Bredig, *J. Am. Chem. Soc.*, 1942, **64**, 1730.

37 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., 1984, vol. 33, p. 203.

38 T. Wilczewski, M. Bochenska, and J. F. Biernat, *J. Organomet. Chem.*, 1981, **87**, 215.

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