Magnetic Circular Dichroism Spectra of Bis(η-cyclopentadienyl)-nickel and -cobalt

By **Trevor J. Barton, Roger Grinter,*** and **Andrew J. Thomson,*** School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

Electronic and magnetic circular dichroism spectra are reported of cobaltocene and nickelocene, $[M(\eta\text{-}C_5H_5)_2]$ (M = Co and Ni), isolated in argon and nitrogen matrices. Most, but not all, of the cobaltocene spectra exhibit a very well developed vibrational fine structure which is attributed to a progression in an e_{2g} vibrational mode which becomes totally symmetric when the symmetry of the molecule is lowered by a Jahn–Teller distortion. No similar effect is clearly visible in the nickelocene spectra but it is suggested that the structure on the long-wavelength bands of both compounds should be attributed to vibronic effects rather than to individual *d–d* transitions. Reasons for the marked similarity between the room-temperature solution and matrix spectra of nickelocene are discussed.

THE electronic structures of the metallocenes have been the subject of much interest for some 25 years and a wide variety of theoretical and experimental studies has been published. In spite of this activity, assignment of the electronic spectra of these compounds still lacks confirmation by other than theoretical calculations, and magnetic circular dichroism (m.c.d.) measurements might be expected to provide useful additional assignment criteria.

For well known reasons, suppression of hot bands, sharpening of the spectra, *etc.*, low-temperature measurements are desirable in both orthodox electronic spectroscopy and in m.c.d. In addition, there are other important advantages to be gained when m.c.d. spectra are measured at low temperatures, particularly in the case of paramagnetic samples.[1] We have therefore measured the m.c.d. spectra of the title compounds in argon and nitrogen matrices at temperatures between 10 and 25 K.

The room-temperature optical spectrum of nickelocene, $[Ni(\eta\text{-}C_5H_5)_2]$, has been reported several times, most recently by Gordon and Warren[2] who have included it in a detailed study of six neutral metallocenes and their 1,1′-dimethyl derivatives. The only low-temperature measurement appears to be that due to Ammeter and Swalen[3] who have published a spectrum recorded at 77 K. It seems to be generally agreed that the three spin-allowed *d–d* transitions (Figure 1) lie under the slightly structured absorption band between 10 000 and 20 000 cm^{-1}, and for an iso-octane solution Gordon and Warren[2] have suggested the assignments given in Table 1.

TABLE 1

Gordon and Warren's[2] assignment of the low-energy region of the electronic spectrum of nickelocene in iso-octane solution

One-electron transition	States	Energy/cm^{-1}
$e_{2g}{}^4a_{1g}{}^2e_{1g}{}^2 \rightarrow e_{2g}{}^4a_{1g}{}^2e_{1g}{}^2$	$^3A_{2g} \rightarrow {}^1A_{1g}$	11 740
$e_{2g}{}^4a_{1g}{}^2e_{1g}{}^2 \rightarrow e_{2g}{}^4a_{1g}e_{1g}{}^3$	$^3A_{2g} \rightarrow {}^3E_{1g}$	14 490
$e_{2g}{}^4a_{1g}{}^2e_{1g}{}^2 \rightarrow e_{2g}{}^3a_{1g}{}^2e_{1g}{}^3$	$^3A_{2g} \rightarrow {}^3E_{2g}$	16 950
$e_{2g}{}^4a_{1g}{}^2e_{1g}{}^2 \rightarrow e_{2g}{}^3a_{1g}{}^2e_{1g}{}^3$	$^3A_{2g} \rightarrow {}^3E_{1g}$	23 040

Until recently, little or no attempt to assign the higher energy bands appears to have been made, but Gordon and Warren[2] have proposed that the strong bands observed in iso-octane solution between 29 000 and 37 000 cm^{-1} be attributed to the $^3A_{2g} \rightarrow {}^3A_{1u}$ ($e_{1g} \rightarrow e_{1u}$) ligand-to-metal charge-transfer transitions. They also suggest that bands at energies above 50 000 cm^{-1} may be assigned to metal-to-ligand charge transfer.

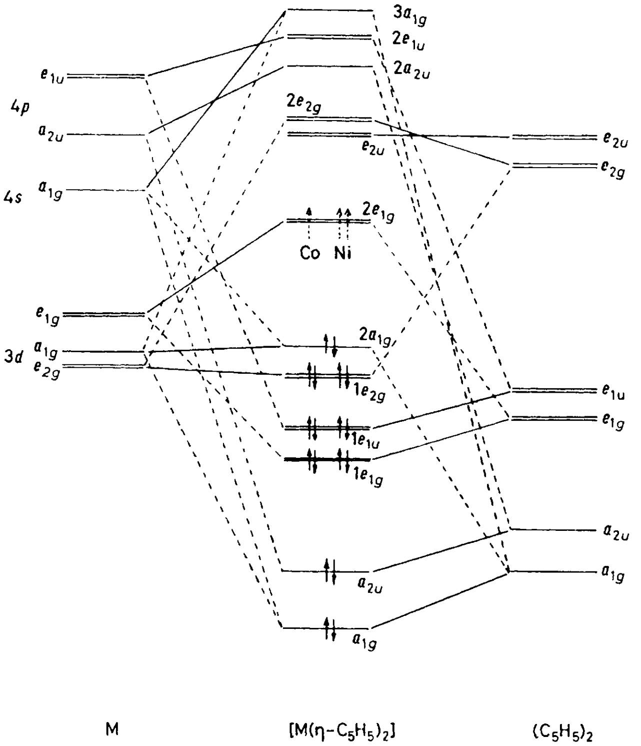

FIGURE 1 Molecular-orbital energy-level scheme for cobaltocene and nickelocene; the energy separations are not to scale

Apart from the papers mentioned above, nickelocene has been the subject of a number of other investigations.[4-6] In contrast, much less work has been reported for cobaltocene. E.p.r. and electronic spectra have been measured by Ammeter and co-workers[3,7] and Gordon and Warren[2] included cobaltocene and 1,1′-dimethylcobaltocene in their recent study. Warren has also reported theoretical work.[8,9] Finally, there is the recent paper on the ligand-field theory, magnetism, and optical spectroscopy of cobaltocene by Konig *et al.*[10]

Gordon and Warren[2] attributed the broad long-wavelength absorption with four shoulders observed for an iso-octane solution of cobaltocene to the spin-allowed *d–d* transitions $^2E_{1g}(e_{2g}{}^4a_{1g}{}^2e_{1g})\rightarrow{}^2A_{1g}$, $^2A_{2g}$, $^2E_{1g}(e_{2g}{}^4a_{1g}e_{1g}{}^2)$ and $^2E_{1g}\rightarrow{}^2A_{1g}$, $^2A_{2g}$, $^2E_{1g}$, and $^2E_{2g}$-$(e_{2g}{}^3a_{1g}{}^2e_{1g}{}^2)$ but they made no detailed assignments of particular bands to specific transitions. Three bands lying between 22 000 and 40 000 cm^{-1} were assigned to ligand-to-metal charge transfer on the basis of shifts to lower energies on methyl substitution. A band at 46 080 cm^{-1} which shows a shift to higher energy was correspondingly assigned as metal-to-ligand charge transfer in nature.

EXPERIMENTAL

Nickelocene and cobaltocene were commercial samples purified by repeated vacuum sublimation. Spectra of the former in deoxygenated, spectroscopic grade cyclohexane were recorded with a Cary 14 spectrophotometer using solutions which had been prepared under nitrogen.

Matrices were obtained by flowing the isolating gas (argon or nitrogen) over solid samples of the metallocenes, the concentration of guest molecules in the matrix being controlled by the rate of gas flow and the temperature of the metallocene. The temperatures used lay in the range 20—40 °C for nickelocene and 30—65 °C for cobaltocene. The matrices were deposited on a sapphire window at the centre of the bore of a 7 T superconducting magnet using a cryostat which has been described elsewhere.[11] M.c.d. spectra of the matrices were recorded using a Cary 61 dichrograph, and absorption spectra were obtained using a Cary 14 in the case of cobaltocene or by recording the dynode voltage of the dichrograph for nickelocene.

Attempts to prepare samples at 10 K yielded opaque, highly scattering matrices. However, at 20 K clear matrices were obtained with both argon and nitrogen; on cooling to 10 K the matrices cracked but they remained clear. They were cycled between 10 and 25 K several times to allow for annealing effects before any temperature-variation studies were attempted.

RESULTS AND DISCUSSION

Cobaltocene.—The cobaltocene matrices obtained were of two distinct types. A blue matrix giving a m.c.d. spectrum showing much well resolved vibrational structure (Figure 2) was the most common result and was found in 14 out of a total of 16 experiments. On two occasions, however, a purple matrix showing very much less structure (Figure 3) was obtained. The matrices obtained using nitrogen as host were always of the blue variety, the two purple matrices being obtained with argon. Changing the concentration of cobaltocene in the matrix by a factor of 10 (as judged by the absorption spectrum) did not change the form of the spectrum and all indications are that both the purple and the blue matrices lie within the same concentration range.

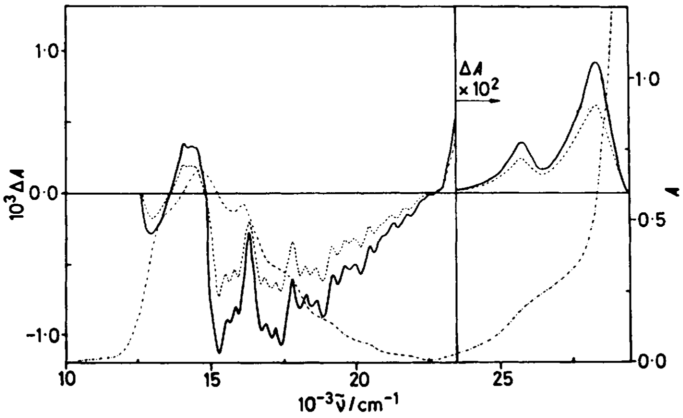

FIGURE 2 Absorption (—·—·—·) and m.c.d. spectra [at 10 (——) and 25 K (- - - - -)] of cobaltocene in a nitrogen matrix; $B = 6.6$ T. These are the spectra of the blue matrix which is normally obtained

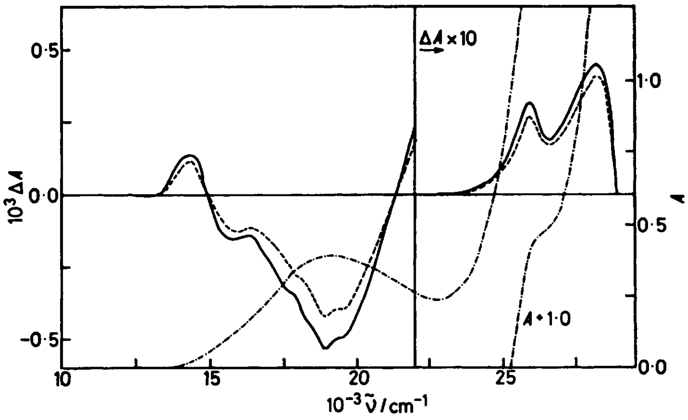

FIGURE 3 Absorption (—·—·—·) and m.c.d. spectra [at 10 (——) and 25 K (– – – –)] of cobaltocene in an argon matrix; $B = 6.6$ T. These are the spectra of the less common purple matrix

The purple absorption spectrum shows almost no vibrational structure, and the low-energy maximum lies at 19 000 cm^{-1} as opposed to 14 500 cm^{-1} for the blue matrix. The m.c.d. spectra of both are similar in form although, as with the absorption spectra, the long-wavelength maximum of the blue form occurs at considerably lower energy than that of the purple form. Above 24 000 cm^{-1} the m.c.d. spectra of both forms are identical, and both show a clear temperature dependence.

The frequencies of the vibronic bands observed and their various separations are in Table 2. If we ignore the longest-wavelength structure, which is not sufficiently clear to measure accurately, we find average separations of 1 340, 425, and 360 cm^{-1}. The vibrations to which these wavenumbers correspond are not, of course, those of the allowed vibration(s). Normally they would be expected to correspond to totally symmetric vibrational modes of the excited state(s) involved. However, in cases such as this where strong Jahn–Teller effects may be present situations can arise in which, because of a Jahn–Teller distortion, a degenerate vibrational mode in the higher symmetry transforms like the totally symmetric mode in the lowered symmetry group and appears as a progression in an electronic spectrum.[12,13]

Examination of the group D_{5h} reveals that the symmetric direct product of E_{1g}, $[E_{1g}]^2$, spans the irreducible representations A_{1g} and E_{2g} while $[E_{2g}]^2$ spans A_{1g} and E_{1g}. We therefore expect that the vibrational spacings which we have observed may correspond to e_{1g} and e_{2g}, as

TABLE 2

The vibrational structure of the m.c.d. spectrum of cobaltocene in a nitrogen matrix at 10 K

Band positions/ cm^{-1}			b–a c–b	Band separations/cm^{-1} a–a	b–b	c–c
1	a	14 020	320			
	b	14 340				
			280			
	c	14 620				
				1 100	1 240	1 310
2	a	15 120				
			460			
	b	15 580				
			350			
	c	15 930				
				1 500	1 450	1 440
3	a	16 620				
			410			
	b	17 030				
			340			
	c	17 370				
				1 370	1 370	1 390
4	a	17 990				
			410			
	b	18 400				
			360			
	c	18 760				
				1 320	1 360	1 370
5	a	19 310				
			450			
	b	19 760				
			370			
	c	20 130				
				1 310	1 280	1 300
6	a	20 620				
			420			
	b	21 040				
			390			
	c	21 430				
				1 260	1 240	1 210
7	a	21 880				
			400			
	b	22 280				
			360			
	c	21 640				
Mean separations excluding set 1			425 360	1 350	1 340	1 340

Overall mean = 1 340

well as a_{1g}, vibrational modes. The most likely candidates would appear to be the following which we take from the work of Hartley and Ware:[14] $\nu_{26}(e_{2g})$ the C–C stretching mode found at 1 358 cm^{-1} in ferrocene and 1 361 cm^{-1} in the cobalticinium ion; $\nu_4(a_{1g})$ the metal–ring stretch found at 311 and 315 cm^{-1} and $\nu_{16}(e_{1g})$ the metal–ring rocking found at 393 and 386 cm^{-1}. As Ammeter and Swalen[3] have pointed out, ν_{26} is expected to be particularly Jahn–Teller active and there seems to be little doubt that our spacing of 1 340 cm^{-1} should be assigned to that vibration. The appearance of this e_{2g} vibration further implies that the electronic band upon which the progression is built has $^2E_{1g}$ as its upper state and corresponds, therefore, to the one-electron transition $(e_{2g}{}^4a_{1g}{}^2e_{1g}) \rightarrow (e_{2g}{}^3a_{1g}{}^2e_{1g}{}^2)$. No such definitive statements may be ventured with regard to the other vibrational spacings observed.

It is tempting to speculate upon the reasons for the appearance of such well developed structure in most of the matrices but not in all. The most plausible explanation would appear to be distortions of the guest molecules by the host. If this occurs, and Ammeter and Brom[7] have shown that such effects can change markedly from one matrix material to another, then we might imagine that in the matrices showing structure the potential high symmetry of the cobaltocene is removed by the Jahn–Teller effect. In the other samples the symmetry is destroyed by the matrix.

One further point may be made with regard to the vibrational structure observed for cobaltocene in a nitrogen matrix. In Table 3 the structure from the absorption spectrum is compared with the data of Gordon and Warren.[2] The structure in the absorption spectrum is much less clear than that in the m.c.d. spectrum (Figure 2) and the tabulated frequencies are therefore very approximate. The similarity of the spacings between the features is, however, quite marked and leads us to conclude that there is no sound experimental basis for assigning the various peaks or shoulders to different electronic transitions. On the whole, our evidence suggests that the long-wavelength absorption is probably dominated by one electronic transition and its associated vibrational structure, both at 20 K and at room temperature. In our opinion the broadness of the band is due to the long vibrational progressions arising from the Jahn–Teller effect[15] rather than from contributions from different electronic transitions.

Turning now to other aspects of the spectra, we note that the slight shoulders in the high-energy regions of the absorption spectra are clearly revealed in the m.c.d. as ΔA maxima at 25 800 and 28 300 cm^{-1}. These bands could correspond to the *d–d* transitions calculated by Warren[8] to lie above 24 000 cm^{-1}. However, in view of their intensity it appears much more reasonable to assign them to ligand-to-metal charge-transfer transitions as Gordon and Warren[2] have done more recently.

The temperature dependence of the m.c.d. of both the blue and the purple matrices shows clearly that we are dealing with a substance having a paramagnetic ground state[1] and, in principle, further information on the nature of these transitions might be obtained by calculation. Unfortunately, a reliable result does not appear to be possible on account of the complexity of the

TABLE 3

Comparison of the absorption spectra of cobaltocene in a nitrogen matrix and in iso-octane solution[2]

In N_2 matrix			In iso-octane	
Absorption peak or shoulder/ cm^{-1}	Differences/ cm^{-1}		Absorption peak or shoulder/ cm^{-1}	Differences/ cm^{-1}
13 300			15 150	
	1 300			1 240
14 600			16 390	
	1 500			1 470
16 100			17 860	
	1 400			
17 500		3 100		3 330
	1 700			
19 200			21 190	
	1 400			
20 600				

problem. We assume that the ground state of the system is the $^2E_1$ (e_1^3) split into two Kramer's doublets with a separation of 127 cm^{-1} by a combination of spin–orbit coupling, static orthorhombic distortion, and dynamic Jahn–Teller effect.[7,10]

The low-energy regions of the spectra show (Figures 2 and 3) $\Delta A/A$ values of the order of 10^{-4} per Tesla, a very low figure which suggests the large B-term contribution to the observed m.c.d. Strong B terms were also observed to dominate the spectrum in the case of ferrocene.[16]

Nickelocene.—Our absorption spectrum of nickelocene in cyclohexane solution is essentially the same as those previously reported.[2,8,17] The m.c.d. spectrum in the same medium is not very informative and quite similar in form to the more detailed matrix spectra. We do not, therefore, reproduce these spectra here.

The m.c.d. spectrum of nickelocene in an argon matrix at 10 K is shown in Figure 4 for the region 10 000—25 000 cm^{-1}. The solution spectrum is blue shifted to 15 000 cm^{-1} and a distinct shoulder appears at *ca.* 17 200 cm^{-1}. Other features occur between 19 000 and 23 000 cm^{-1} but these are extremely weak. The other major features are at 23 800 and 25 000 cm^{-1}. An attempt was made to study the temperature variation of these weak bands but no reproducible results could be obtained. The absorption spectrum, as measured by the dynode voltage of the dichrograph, showed no peak in the region.

The corresponding spectra for the region 25 000—45 000 cm^{-1} are reproduced in Figure 5. Two m.c.d. spectra are shown, one at 10 K and the other at 20 K. The m.c.d. in the matrix consists of two positive bands at 29 800 and 32 900 cm^{-1}, associated with the two absorption bands, and a broad band with positive ΔA at *ca.* 37 500 cm^{-1}. The absorption spectrum in the matrix corresponds closely with the solution spectrum with bands blue shifted by some 600 cm^{-1}. The highest energy solution band at 36 400 cm^{-1} might be expected to appear at *ca.* 37 000 cm^{-1} in the matrix, but it is not seen. The striking similarity between the solution and matrix spectra requires further comment.

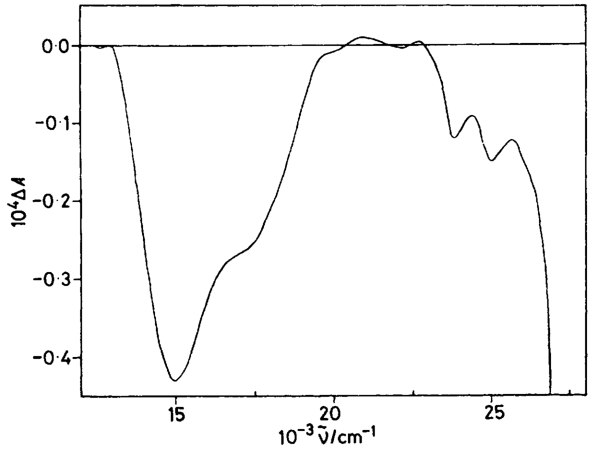

FIGURE 4 M.c.d. spectrum of nickelocene in an argon matrix at 10 K; B = 6.6 T

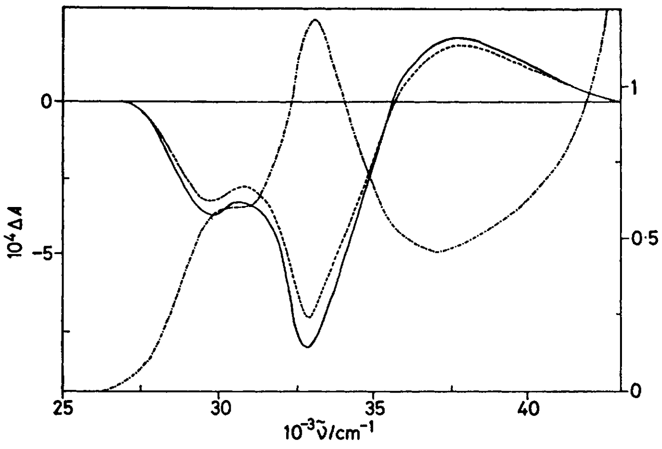

FIGURE 5 Absorption (— · — · —·) and m.c.d. spectra [at 10 (——) and 20 K (– – – –)] of nickelocene in an argon matrix, B = 6.6 T

The magnetic susceptibility studies of Prins and co-workers[4,5] showed that the $^3A_{2g}$ ground state of nickelocene is subject to a zero-field splitting of *ca.* 26 cm^{-1} giving A_1 and E_1 states of which the former is the lower in energy. The resulting scheme for the low-energy optical transitions is complicated but at very low temperatures only the A_1 level will be significantly populated whereas at room temperature the populations of the A_1 and E_1 states should be approximately equal. Thus one might expect marked differences between the spectra at room temperature and 10 K, but this is not observed in practice.

The temperature dependence of the m.c.d. is not the simple $1/T$ function expected as is shown by the figures quoted in Table 4. The results give measurements made at the fixed energies 29 800, 32 900, and 37 500 cm^{-1}. Magnitudes were obtained by measuring the difference between the m.c.d. signals obtained with the normal and reversed magnetic fields and the reproducibility was checked periodically by a return to previously measured conditions.

The absence of significant temperature dependence in the long-wavelength portion of the m.c.d. spectrum is unexplained. Possibly it is due to the fact that it is dominated by the broad band at 15 000 cm^{-1}, which is mainly due to a B term, obscuring other spectral changes of closely spaced bands. Unfortunately, a detailed calculation of the expected signs of the C terms of bands due to *d–d* transitions is not possible. The bands have vibronic intensity and the signs of the C terms are totally dependent upon the symmetry of the allowed vibration and also upon the symmetry of the electronic state.

TABLE 4

The magnitude of ΔA for the three m.c.d. maxima of nickelocene in an argon matrix at several temperatures

Temperature (T/K)	$\lvert\Delta A\rvert$ (arbitrary units)		
	29 800 cm^{-1}	32 900 cm^{-1}	37 500 cm^{-1}
10	0.30	0.76	0.275
20	0.275	0.70	0.25
30	0.25	0.595	0.23
40	0.235	0.535	

Therefore, without a knowledge of or an assumption concerning one or the other of these factors a clear prediction does not emerge. A somewhat similar situation was encountered in the interpretation of the m.c.d. spectrum of matrix-isolated ferrocene.[16] As far as the high-energy region of the spectrum is concerned, the absence of oppositely signed m.c.d. bands suggests orbitally non-degenerate excited states and therefore provides support, albeit of a negative character, for Gordon and Warren's [2] assignment as ligand-to-metal charge-transfer transitions, $^3A_{2g} \rightarrow {}^3A_{1u}$.

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REFERENCES

[1] P. N. Schatz and A. J. McCaffery, *Quart. Rev.*, 1970, **23**, 552; P. J. Stephens, *Ann. Rev. Phys. Chem.*, 1974, **25**, 201.

[2] K. R. Gordon and K. D. Warren, *Inorg. Chem.*, 1978, **17**, 987.

[3] J. H. Ammeter and J. D. Swalen, *J. Chem. Phys.*, 1972, **57**, 678.

[4] R. Prins, J. D. W. Van Voorst, and C. J. Schinkel, *Chem. Phys. Letters*, 1967, **1**, 54.

[5] R. Prins and J. D. W. Van Voorst, *J. Chem. Phys.*, 1968, **49**, 4665.

[6] R. Prins, *J. Chem. Phys.*, 1969, **50**, 4804.

[7] J. H. Ammeter and J. M. Brom, *Chem. Phys. Letters*, 1974, **27**, 380.

[8] K. D. Warren, *J. Phys. Chem.*, 1973, **77**, 1681.

[9] K. D. Warren, *Inorg. Chem.*, 1974, **13**, 1317.

[10] E. König, R. Schnakig, S. Kremer, B. Kanellakopulos, and R. Klenze, *Chem. Phys.*, 1978, **27**, 331.

[11] T. J. Barton, R. Grinter, and A. J. Thomson, *J.C.S. Dalton*, 1978, 608.

[12] M. H. L. Pryce and W. A. Runciman, *Discuss. Faraday Soc.*, 1958, **26**, 34.

[13] R. A. Ford and O. F. Hill, *Spectrochim. Acta*, 1960, **16**, 493.

[14] D. Hartley and M. J. Ware, *J. Chem. Soc. (A)*, 1969, 138.

[15] H. C. Longuett-Higgins, U. Öpik, M. H. L. Pryce, and H. Sack, *Proc. Roy. Soc.*, 1958, **A244**, 1.

[16] T. J. Barton, I. N. Douglas, R. Grinter, and A. J. Thomson, *J.C.S. Dalton*, 1976, 1948.

[17] D. R. Scott and R. S. Becker, *J. Chem. Phys.*, 1961, **35**, 516.