Inorg. Chem. 1981, 20, 525–527

Contribution from the Department of Chemistry,
University of Leicester, Leicester LE1 7RH, England

Far-Infrared Spectrum of Oriented Crystals of Bis(dimethylglyoximato)nickel(II)

DAVID M. ADAMS* and DAVID C. STEVENS

Received May 23, 1980

The out-of-plane modes of $Ni(dmg)_2$ have been identified and distinguished from in-plane modes by direct observation using oriented crystals in polarized radiation (20–600 cm^{-1}). A full assignment of the out-of-plane skeletal modes is offered.

Introduction

In the assignment of the vibrational spectra of planar complexes, one of the least accessible pieces of evidence is that which allows a distinction to be made between vibrations which take place in the plane of the molecule and those in which the atom displacements are perpendicular to the molecular plane. There are examples in the literature in which assignments have been made quite arbitrarily to the two types of mode, even as a basis for normal coordinate analysis. Since the out-of-plane modes are usually skeletal deformations, they tend to be low in frequency and sensitive to the particular structure type. There is, therefore, a considerable need for direct determination of out-of-plane modes by single–crystal IR spectroscopy. We have previously reported such work for K_2PtCl_4,[1] K_2PtBr_4,[2] $Rh(CO)_2acac$,[3] and $VO(acac)_2$.[4] We now give the results of a far-infrared study of $Ni(dmg)_2$ (dmg = dimethylglyoximato).

This material has been studied previously by IR spectroscopy,[5–10] usually because of its interest as a probable example of a symmetrical hydrogen bond. No far-infrared or Raman data exist, and there have been no single-crystal investigations of its vibrational spectra, although the anisotropy of both its electronic spectra[11] and its electrical conduction[12] have been examined.

Theory

$Ni(dmg)_2$ crystallizes with the symmetry of space group $Ibam = D_{2h}^{26}$ with a bimolecular primitive cell.[13] The molecules are crystallographically required to have symmetry C_{2h} but are said to be D_{2h} within the limits of structure determination. The planar molecules are stacked along the c axis with alternate molecules separated by $c/2$ and rotated by $\pi/2$ relative to each other. Thomas and Underhill[14] have shown that this form of packing is assisted by interlocking of the methyl groups on successive molcules.

Since our study is restricted to the region <600 cm^{-1}, the motions of the protons in the O---H---O bonds may be neglected as they are at higher frequencies, as are also the modes of the methyl groups, other than the torsions. On this basis each molecule has 45 normal modes distributed as shown in Table I. These modes couple via the site field to yield a vector of 90 modes for the two molecules in the primitive cell. In addition there are optic branch lattice modes which span the representations

$$\text{libratory} \quad A_g + B_{1g} + 2\,B_{2g} + 2\,B_{3g}$$

$$\text{translatory} \quad A_u + B_{2u} + B_{3u}$$

Table I. Mode Analysis for $Ni(dmg)_2$ (Hydrogen Atoms Omitted)

	molecule D_{2h}	site $C_{2h}(z)$ $\xrightarrow{\times 2}$	crystal D_{2h}^{16}
ν_{1-8}	$8a_g$	$15A_g$	$15(A_g + B_{1g})$
ν_{9-15}	$7b_{1g}$		
ν_{16-18}	$3b_{2g}$	$6B_g$	$6(B_{2g} + B_{3g})$
ν_{19-21}	$3b_{3g}$		
ν_{22-25}	$4a_u$	$8A_u(c)$	$8(A_u + B_{1u})$
ν_{26-29}	$4b_{1u}(z)$		
ν_{30-37}	$8b_{2u}(y)$	$16B_u(a, b)$	$16(B_{2u} + B_{3u})$
ν_{38-45}	$8b_{3u}(x)$		

The g modes are all Raman active and are not dealt with in this paper as we have been unable to obtain useable single-crystal Raman data due to burning in the laser beam. A_u modes are inactive in D_{2h}, but the B_{nu} modes (n = 1–3) are all IR active. Specifically, B_{1u} modes may be excited with the electric vector parallel to c and represent out-of-plane molecular modes. B_{2u} and B_{3u} modes, which may be selectively excited with **E** perpendicular to c, are in-plane modes.

The crystals used in this work were in the form of very thin needles elongated along the c axis. Although good dichroic data were obtained for **E** both parallel and perpendicular to the c axis, it was impossible to obtain (001) sections. We were unable therefore to distinguish between B_{2u} and B_{3u} crystal modes, which appear together in the **E** perpendicular to c spectrum. In fact, this is not a serious deficiency. Each in-plane mode has the strict symmetry B_u (in C_{2h}) although the D_{2h} classification into B_{2u} and B_{3u} species is likely to be a very good approximation. The difference between the crystal (D_{2h}^{16}) species B_{2u} and B_{3u} arises because the correlation field allows coupling of the corresponding B_u modes of the two molecules in the cell. However, these two molecules are at right angles to each other, and the coupling between the two B_u modes will be zero. Hence the B_{2u} and B_{3u} modes arising from this coupling will have nearly identical energies. It follows that $\mathbf{E}\|a$ and $\mathbf{E}\|b$ experiments would not yield spectra differing either from each other or from their sum ($\mathbf{E}\perp c$), at least insorfar as internal modes are concerned. Thus, we expect to find a total of 16 (ν_{30-45}) skeletal modes in the $\mathbf{E}\perp c$ spectrum rather than the 16 pairs implied by the right-hand column of Table I.

Only the torsional modes of the methyl groups are low enough in energy to appear at <600 cm^{-1}. Their representation may be deduced by

	C_{3v} (isolated group)	$C_s\,(xy)$	D_{2h} (molecule)
$\tau(CH_3)$	a_2	A''	$B_{2g} + B_{3g} + A_u + B_{1u}$

---

(1) D. M. Adams and D. C. Newton, *J. Chem. Soc. A*, 2998 (1969).

(2) D. M. Adams and D. J. Hills, *J. Chem. Soc., Dalton Trans.*, 947 (1977).

(3) D. M. Adams and W. R. Trumble, *J. Chem. Soc., Dalton Trans.*, 690 (1974).

(4) D. M. Adams and W. R. Trumble, *Inorg. Chim. Acta*, **13**, 17 (1975).

(5) R. C. Voter, C. V. Banks, V. A. Fassel, and P. W. Kehres, *Anal. Chem.*, **23**, 1730 (1951).

(6) R. E. Rundle, R. C. Voter, and C. V. Banks, *J. Chem. Phys.*, **19**, 1205 (1951).

(7) R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

(8) R. Blinc and D. Hadzi, *J. Chem. Soc.*, 4536 (1958).

(9) R. Blinc and D. Hadzi, *Spectrochim. Acta*, **16**, 853 (1960).

(10) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).

(11) S. Yamada and R. Tsuchida, *J. Am. Chem. Soc.*, **75**, 6351 (1953).

(12) P. S. Gomm, T. W. Thomas, and A. E. Underhill, *J. Chem. Soc. A*, 2154 (1971).

(13) L. E. Godycki and R. E. Rundle, *Acta Crystallog.*, **6**, 487 (1953).

(14) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1971).

0020-1669/81/1320-0525$01.00/0

Table II. IR Wavenumbers (in cm^{-1}) (<600 cm^{-1}) for Ni(dmg)$_2$ and Their Assignment

mull[a]		E‖*c*[b]		E⊥*c*[b]			
295 K	100 K	295 K	100 K	295 K	100 K	assignt	possible major contributions
49 ± 2 (vvw, sh)	54 ± 1 (vw)			50 ± 3	55 ± 2	B_{2u} or B_{3u}	ν_L
59 ± 1 (vw, sh)	68 (m)	58	67.5			B_{1u}	ring deformn
82 (m)	84 (vs)			82	83	B_{3u} or B_{2u}	ν_L
	191 (vvs)			183	187.5	B_{2u}, B_{3u}	ring deformn
						B_{2u}, B_{3u}	δ(C–CH$_3$)
187 (vs, b)	200 (vvs)	196	201	192	200	B_{1u}	τ(CH$_3$)
270 (s)	272.5 (vvs)			269	272	B_{2u}, B_{3u}	δ(Ni–N)
295 (m, b)	300 (vvs)	294	300	(295)?	300	B_{1u}	π(Ni–N)
323 ± 1 (w, vb)	327.5 (m)	321	327			B_{1u}	
405 (m)	406 (s)	(404 ± 2)	(406 ± 2)	405	406	B_{2u}, B_{3u} (B_{1u})	δ(N–O)
429 (vs)	432 (vvs)	428 ± 2	430 ± 2			B_{1u}	π(C–CH$_3$)
	(475 ± 5)? (w, b sh)				(470 ± 5)?	(B_{2u}, B_{3u}?)	
496 ± 1	497 (vs, b)	495 ± 2	497 ± 2			B_{1u}	π(N–O)
521 (vvs)	523 (vvs)			520	522	B_{2u}, B_{3u}	ν(Ni–N)

[a] All bands ±0.5 cm^{-1} unless otherwise indicated. [b] Single crystal; all bands ±1 cm^{-1} unless otherwise indicated.

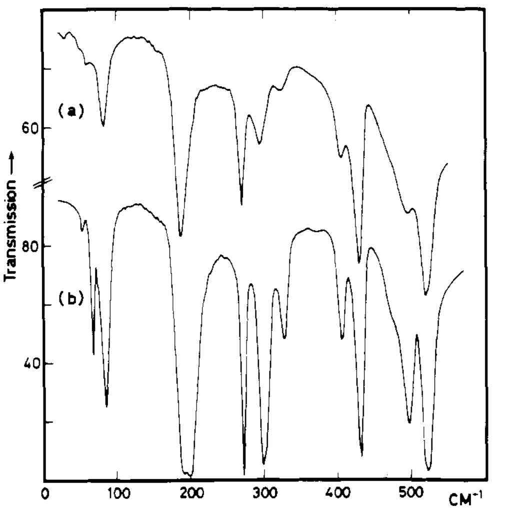

Figure 1. Far-infrared spectra of Nujol mulls of Ni(dmg)$_2$ at (a) 295 K and (b) 100 K.

where C_s (xy) is the site symmetry of methyl in the complex. Coupling of the A_u and B_{1u} modes of the two molecules per cell yields, finally, 2(A_u + B_{1u}). Hence two τ(CH$_3$) modes are permitted in the E‖*c* but none in the E⊥*c* spectrum.

Experimental Section

Ni(dmg)$_2$ was prepared by a standard method.[15] Crystals were grown from hot nitrobenzene by cooling in air and had the form of very thin needles (<0.1 mm) of up to 10 mm length parallel to the *c* axis. About 20 of the smaller crystals were mounted close together across a 1 mm diameter hole in a copper disk and fixed with a thin film of silicone grease. The disk was mounted on the end of a cryostat. Supplementary work was done by using Nujol mulls. Essentially the same spectra resulted from samples with crystals of various widths. Accordingly we conclude that any polarization effects arising from the crystal grid itself are negligible.

IR spectra were obtained by using a Beckman-RIIC FS-720 interferometer and a polyethylene-based wire-grid polarizer.

Results and Discussion

Results are summarized in Table II and Figures 1 and 2. The IR spectra showed good but not quite perfect extinctions between runs with the electric vector parallel or perpendicular to the *c* axis. This is hardly surprising in view of the sample used. Nevertheless, the data generally leave little doubt about the symmetry of a given mode.

(a) Out-of-Plane Modes. The E‖*c* Spectrum. No lattice modes are allowed in the B_{1u} spectrum. The spectrum should show eight internal skeletal modes, which originate from ν_{22-25} (a_u) and ν_{26-29} (b_{1u}) in the individual molecules. On the supposition that a_u and b_u modes associated principally with a given internal coordinate set will appear in reasonable proximity, we look for four *regions* of absorption, to which must be added a fifth due to the two methyl torsions.

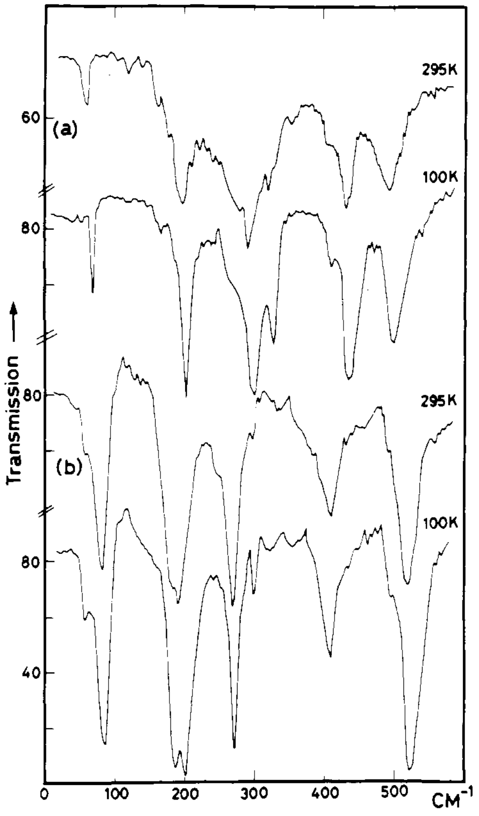

Figure 2. Single-crystal IR transmission spectra of Ni(dmg)$_2$ in polarized light with the electric vector (a) parallel and (b) perpendicular to the crystal *c* axis.

In the region 20–600 cm^{-1}, six bands appeared in the E‖*c* spectrum with a seventh (405 cm^{-1}) possibly also having B_{1u} character. In mull spectra all but one (429 cm^{-1}) of these seven bands were further distinguished by showing very pronounced sharpening as the temperature was lowered. These bands occur, as predicted, in five fairly well-separated regions.

Exact descriptions of all these modes must await further experimental evidence from isotopically substituted variants, followed (not preceded) by normal coordinate analysis. However, it is clear which sets of internal coordinate will contribute to B_{1u} modes. They are, respectively, the out-of-

---

(15) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis", Longmans, London, 1961.

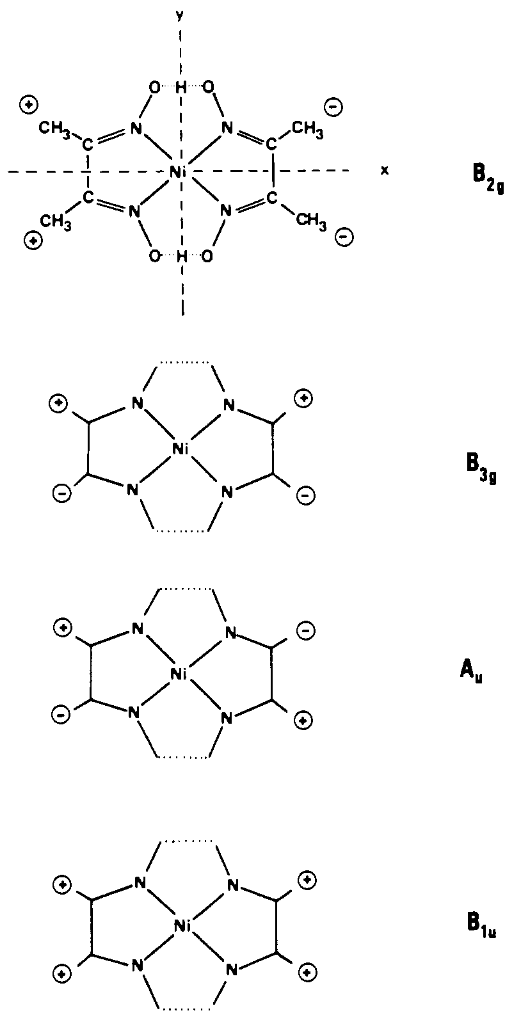

Figure 3. Forms of the vibrational modes for the (hypothetical) case of pure $\pi(C-CH_3)$ deformation.

plane motions of the $C-CH_3$, N–O, and Ni–N bonds, complex ring deformational motions involving the whole skeleton, and methyl torsions. These motions, combined with respect to symmetry, are illustrated in Figure 3 for the hypothetical case of modes involving pure $\pi(C-CH_3)$ motion.

The lowest B_{1u} mode (59 cm^{-1}) may safely be attributed to the complex deformational mode ν_{29}. Methyl torsions are assigned to absorption ~190 cm^{-1}. The three remaining mode types involve out-of-plane motion of N–O, $C-CH_3$, and Ni–N bonds. Of these π(N–O) is likely to be the highest and π(Ni–N) the lowest. Any other assignment would imply that ν(Ni–N) is unrealistically high. The assignment is summarized in Table II. We note that two of the three higher energy regions of absorption each definitely or probably contains two bands, in accord with theory.

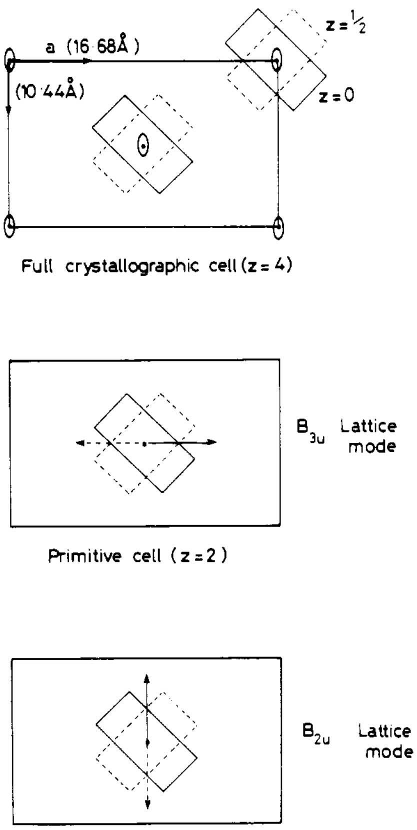

Figure 4. Forms of the B_{2u} and B_{3u} translatory lattice modes of $Ni(dmg)_2$.

(b) In-Plane Modes. The E⊥c Spectrum. The two predicted translatory modes, in which the molecules move relative to each other in *ab* planes, Figure 4, are assigned at 49 and 82 cm^{-1}, respectively. There is then a gap in the in-plane spectrum until 187 cm^{-1} whereupon a series of internal skeletal mode absorptions begins. This series should consist of 16 bands (each bearing B_{2u} and B_{3u} labels), but some members of it will unquestionably be >600 cm^{-1} (e.g., $\nu_{C=N}$). Therefore, at this point we note simply that bands <600 cm^{-1} with in-plane character have been identified. The assignment of ν(Ni–N) at 521 cm^{-1} is supported by a recent isotopic shift study[16] which shows that in $[Co(dmg)_2(py)Cl]$ ν(Co–N(dmg)) is at 512 cm^{-1}.

Acknowledgment. We thank the SRC for a grant to D.C.S. and for other support.

Registry No. $Ni(dmg)_2$, 13478-93-8.

---

[16] P. E. Rutherford and D. A. Thornton, *Spectrochim. Acta, Part A*, **35A**, 711 (1979).