approximate to linearity ($Mo_1-C_{17}-O_2$ = 177.9 ± 1.7°, $Mo_2-C_{20}-O_5$ = 179.4 ± 1.7°) whereas the remaining four Mo–C–O angles vary from 171.5 ± 1.7 to 176.3 ± 1.7°. [Nonlinearity of M–C–O groups is, of course, expected for carbonyl ligands in environments of low symmetry[34] and may also result from the known close *intra*molecular and *inter*molecular contacts.]

Since both π-cyclopentadienyl and π-pentadienyl groups may be regarded as formally tridentate, six-electron donors, the present molecule contains two seven-coordinate molybdenum atoms. The coordination geometry of the metal atoms is related to that in the seven-coordinate species $\pi\text{-}C_5H_5Mo(CO)_3C_2H_5$,[35] $\pi\text{-}C_5H_5Mo(CO)_3C_3F_7$,[36,37] $\pi\text{-}C_5H_5Mo(CO)_3COCF_3$,[38] $[\pi\text{-}C_5H_5Mo(CO)_3]_2$,[32] $\pi\text{-}C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$,[39] $\pi\text{-}C_5H_5Mo(CO)_3CH_2CO_2H$,[40] $[C_{10}H_8Mo(CO)_3CH_3]_2$,[11,12] $[\pi\text{-}C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}\{H\}$,[41] and $\pi\text{-}C_5H_5Mo(CO)_3\text{-}Sn(\pi\text{-}C_5H_5Fe(CO)_2)_2Cl$.[42] A unique feature of the present structure is the large *trans*-Mo–Mo–CO angle of ~160°. In each of the complexes mentioned previously, the corresponding R–Mo–CO or Mo–Mo–CO angle is only ~130°.

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(34) S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965).

(35) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

(36) M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 695 (1966).

(37) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

(38) M. R. Churchill and J. P. Fennessey, unpublished work.

(39) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

(40) M. L. H. Green, J. K. P. Ariyante, A. M. Bjerrum, M. Ishaq, and C. K. Prout, *Chem. Commun.*, 430 (1967).

(41) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

(42) J. E. O'Connor and E. R. Corey, *ibid.*, **89**, 3930 (1967).

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The Crystal and Molecular Structure of Bis(2,4-pentanedionato)bis(pyridine N-oxide)nickel(II), $Ni(C_5H_7O_2)_2(C_5H_5NO)_2$[1a]

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The structure of bis(2,4-pentanedionato)bis(pyridine N-oxide)nickel(II), $Ni(C_5H_7O_2)_2(C_5H_5NO)_2$, has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, space group C2/c, with a = 14.653 ± 0.005 Å, b = 16.972 ± 0.005 Å, c = 18.344 ± 0.005 Å, and β = 100.74 ± 0.05°. For Z = 8 the measured and calculated densities are 1.32 and 1.324 g/cm,^{3} respectively. Counter data were collected for 2319 independent reflections by the θ–2θ scan technique. The structure was refined, including hydrogens, by least-squares methods to a conventional R value of 0.097. The six oxygen atoms coordinated to the nickel are in nearly regular octahedral disposition with the pyridine N-oxide molecules *cis* to one another and so inclined as to make an average Ni–O–N angle of 121°.

Introduction

Heterocyclic amine N-oxides act as oxygen donor ligands in a variety of transition metal coordination compounds.[2] Very recently structural studies have been reported for compounds which involve pyridine N-oxide acting as a bridging ligand between copper atoms;[3–5] however, no other structural work dealing with complexes of this class of ligand appears to have been done. Not long ago Kluiber and Horrocks[6,7] synthesized and studied complexes of the type bis(2,4-pentanedionato)bis(heterocyclic amine N-oxide)metal(II), hereafter referred to as $M(AA)_2(ligand)_2$, where M = Co, Ni. These complexes belong to the class of neutral donor adducts of $M(AA)_2$ of which the dihydrates,[8,9] $M(AA)_2(H_2O)_2$, and dipyridinates,[10] $M(AA)_2(C_5H_5N)_2$, are known and which involve *trans*-octahedral coordination of the metal in the solid state. On the basis of an analysis of the dipolar (pseudocontact) contribution to the isotropic proton magnetic resonance shifts in solution in the complexes $M(AA)_2(L)_2$ (M = Co or Ni; L = pyridine N-oxide or γ-picoline N-oxide), Kluiber and Horrocks[6] estimated an average M–O–N angle in the range 115–130° for the coordinated heterocyclic amine N-oxides.[11] These results were based on a *trans*-octahedral model for co-

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(2) See, for example, D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966); M. R. Kidd, R. S. Sager, and W. H. Watson, Jr., *ibid.*, **6**, 946 (1967); P. D. Kaplan and M. Orchin, *ibid.*, **6**, 1096 (1967); F. E. Dirkson, E. W. Gowling, and F. F. Bentley, *ibid.*, **6**, 1099 (1967), and references therein.

(3) S. Šćavničar and B. Matković, *Chem. Commun.*, 297 (1967).

(4) R. S. Sager, R. J. Williams, and W. H. Watson, Jr., *Inorg. Chem.*, **6**, 951 (1967).

(5) H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(6) R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965).

(7) R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

(8) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

(9) H. Montgomery and E. C. Lingafelter, *ibid.*, **17**, 1481 (1964).

(10) J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965). The complete crystal structure of *trans*-$Co(AA)_2(C_5H_5N)_2$ has recently appeared: R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

(11) A similar estimate was later, but apparently independently, made for the same systems: E. E. Zaev and U. N. Molin, *J. Struct. Chem.* (U.S.S.R.), **7**, 680 (1966).

ordination which was suggested by the known solid-state structures[8-10] for the compounds with L = H_2O, C_5H_5N. Clearly, the detailed geometry of the coordination of heterocyclic amine N-oxides in general and the stereochemistry of $M(AA)_2(C_5H_5NO)_2$ in particular are of interest. The present article reports the results of the crystal and molecular structure determination of $Ni(AA)_2(C_5H_5NO)_2$. Earlier powder X-ray work[6] showed the analogous cobalt complex to crystallize in two modifications, one of which was isomorphous and presumably isostructural with the nickel compound.

Experimental Section

Crystals of bis(2,4-pentanedionato)bis(pyridine N-oxide)-nickel(II), $Ni(C_5H_7O_2)_2(C_5H_5NO)_2$, were prepared by the method of Kluiber and Horrocks.[6] The bright green crystals were of irregular habit; the external morphology provided little clue as to the directions of the crystal axes. A crystal of approximate dimensions 0.16 × 0.15 × 0.80 mm was chosen for intensity measurements and was mounted on a quartz fiber with the b axis (unique) of the monoclinic cell parallel to the spindle axis of the instrument. The unit cell dimensions were determined at room temperature on a General Electric XRD-5 unit equipped with a manual goniostat, scintillation counter, and pulse height discriminator using unfiltered molybdenum radiation (λ 0.70926 Å for $K\alpha_1$). They are $a = 14.653 \pm 0.005$ Å, $b = 16.972 \pm 0.005$ Å, $c = 18.344 \pm 0.005$ Å, and $\beta = 100.74 \pm 0.05°$. Systematic absences on Weissenberg film layers $h0l$ through $h3l$ were: for hkl, $h + k = 2n + 1$; for $h0l$, $l = 2n + 1$; these imply space group Cc or C2/c. The density measured by flotation in a carbon tetrachloride–methylcyclohexane mixture was 1.32 ± 0.01 g/cm^3 which compares favorably with the calculated density of 1.324 g/cm^3 for $Z = 8$. With eight molecules per unit cell and the appearance of $2x$, $2y$, $2z$ peaks for nickel in the Patterson function, the centric space group C2/c (C_{2h}^6, no. 15) was chosen and this choice was confirmed by the subsequent refinement of the structure. All atoms occupy general positions and no molecular symmetry conditions are imposed by crystallographic symmetry.

Although the structure was actually solved using data obtained by 10-sec peak counts on the manual goniostat and employing zirconium-filtered molybdenum radiation and a 4° take-off angle, intensity data for the final refinement reported here were recorded on an automated GE XRD-5 diffractometer. Nickel-filtered (at the receiving slit) copper radiation (λ 1.54051 Å for $K\alpha_1$) with a 20-mA source current, a 2° take-off angle, and a θ–2θ scan technique were employed. Scans commenced at 2θ values 0.7° below the calculated $K\alpha_1$ position, proceeded through the $K\alpha_1$–$K\alpha_2$ separations, to 0.7° beyond the $K\alpha_2$ peak position at a rate of 1°/min. A 10-sec background count was taken 0.4° from each end of the peak scan. The background correction for each reflection was obtained from the average of the two background counts pro-rated to the duration of the peak count. In order to assess the importance of counter saturation, the reflections with $2\theta \leq 50°$ were remeasured with a source current of 6 mA. Only the most intense reflection was appreciably affected by errors from this cause. The 6-mA data were averaged with the 20-mA data using a scale factor obtained from a comparison of 40 representative reflections of intermediate intensity obtained at both amperages. Of the 2319 nonequivalent reflections measured, 2113 were observed to be nonzero. A zero intensity was recorded whenever a count was less than or equal to the background recorded for that particular reflection. The corrected intensities, I, were assigned standard deviations according to the formula

$$\sigma(I) = [\mathrm{TC} + 0.25(t_c/t_b)^2(B_1 + B_2) + (0.05I)^2]^{1/2}$$

where TC is the total integrated peak count obtained in a scan time t_c, B_1 and B_2 are the two background counts each obtained in time t_b, and $I = \mathrm{TC} - 0.5\,(t_c/t_b)(B_1 + B_2)$. Six standard reflections were recorded every 100 measurements. The constancy of these reflections indicated little or no deterioration of the crystal during data collection. The linear absorption coefficient of the crystal using Mo $K\alpha$ is $\mu = 15.1$ cm^{-1}. No noticeable absorption effects appeared for any $0k0$ reflections as a function of ϕ rotation and no absorption corrections were applied to the data.

Solution and Refinement of the Structure

A three-dimensional Patterson[12] synthesis located the nickel and several of the adjacent oxygens. A least-squares refinement and subsequent Fourier synthesis[12] disclosed the remaining atoms. Least-squares refinement proceeded with all 29 nonhydrogen atoms and only the nickel atom treated anisotropically to a conventional R value[13] of 0.117. At this point a difference synthesis disclosed all but one of the 24 hydrogens. When the hydrogens were included and refined, R dropped to a final value of 0.097 for all reflections. The error in an observation of unit weight at the end was 2.49. Atomic scattering factors and dispersion corrections were taken from the "International Tables."[14] The isotropic thermal parameters have the form $\exp[-B(\sin^2\theta)/\lambda^2]$ while the anisotropic temperature factor was

$$\exp[-0.25(B_{11}b_1{}^2h^2 + B_{22}b_2{}^2k^2 + B_{33}b_3{}^2l^2 + 2B_{12}b_1b_2hk + 2B_{13}b_1b_3hl + B_{23}b_2b_3kl)]$$

where b_i is the ith reciprocal axis. The values of the hydrogen coordinates and their temperature factors obtained from the final refinement are [hydrogen, x, y, z (temperature factor)]: H(1A), 0.272, −0.183, 0.104 (12.6); H(1B), 0.348, −0.143, 0.099 (−1.1); H(1C), 0.278, −0.117, 0.141 (1.1); H(3), 0.179, −0.177, −0.013 (2.9); H(5A), 0.038, −0.170, −0.114 (5.4); H(5B), 0.058, −0.132, −0.176 (1.2); H(5C), 0.112, −0.187, −0.164 (4.5); H(6A), 0.424, 0.047, −0.189 (−1.5); H(6B), 0.485, 0.114, −0.136 (1.8); H(6C), 0.435, 0.148, −0.197 (5.0); H(8), 0.307, 0.191, −0.193 (4.8); H(10A), 0.065, 0.246, −0.196 (6.0); H(10B), 0.167, 0.250, −0.232 (10.8); H(10C), 0.112, 0.218, −0.227 (−1.2); H(11), 0.043, −0.030, 0.069 (−1.5); H(12), 0.048, −0.079, 0.168 (−0.7); H(13), 0.157, −0.022, 0.263 (5.9); H(14), 0.205, 0.082, 0.278 (2.6); H(15), 0.200, 0.115, 0.127 (0.9); H(16), 0.363, 0.271, −0.001 (1.1); H(17), 0.509, 0.274, 0.008 (5.0); H(18), 0.586, 0.183, 0.076 (1.0); H(19), 0.542, 0.106, 0.081 (1.7); H(20), 0.418, 0.074, 0.065 (10.5).

The hydrogen-labeling scheme should be obvious from Figure 1; however, not much significance should

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(12) Computations were performed on IBM 7044 and CDC 6600 computers at Lawrence Radiation Laboratory. The following computer programs were used for the operations indicated: instrumental setting: Zalkin's GONIO (a modification of a program written by Larsen) and EULERA; reduction of raw data: Zalkin's AUDIT and INCOR; Patterson and Fourier synthesis: Zalkin's FORDAP; least-squares refinement: Zalkin's LS 250 (a modification of the Gantzel–Sparks–Trueblood full-matrix program which minimizes $\Sigma w|\Delta F|^2/\Sigma w|F_o|^2$, $w = 1/\sigma^2(F)$); interatomic distance and angle computation: Zalkin's DISTAN; calculation of least-squares planes: Chu's LSPLAN; graphical representation of atomic positions and molecular stereochemistry: Zalkin's ATMPLT and Johnson's ORTEP; preparation of Table I: Zalkin's LIST.

(13) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(14) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 201 ff.

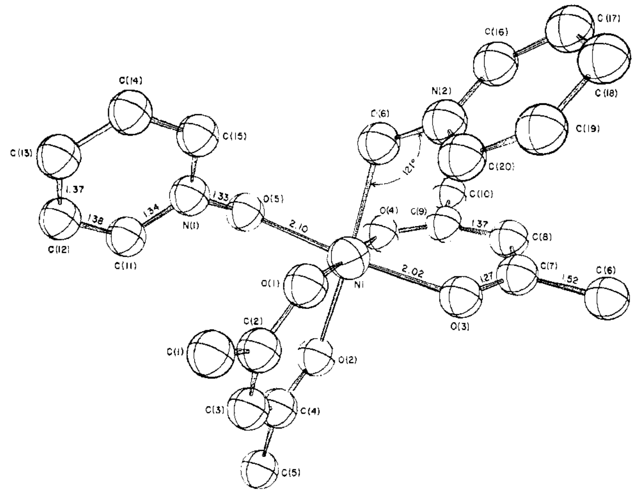

Figure 1.—Geometry of $Ni(AA)_2(C_5H_5NO)_2$ with the average values of chemically equivalent bond lengths indicated.

be attached to the numerical values of these parameters. In some instances considerable displacement of the hydrogen from the position expected on the basis of the heavy-atom structure was noted. The calculated C–H distances ranged from 0.62 to 1.09 Å with an average of 0.83 Å and an estimated standard deviation of ±0.13. Since the hydrogen positions in the present structure are of no particular chemical interest, no further consideration will be given to them here.

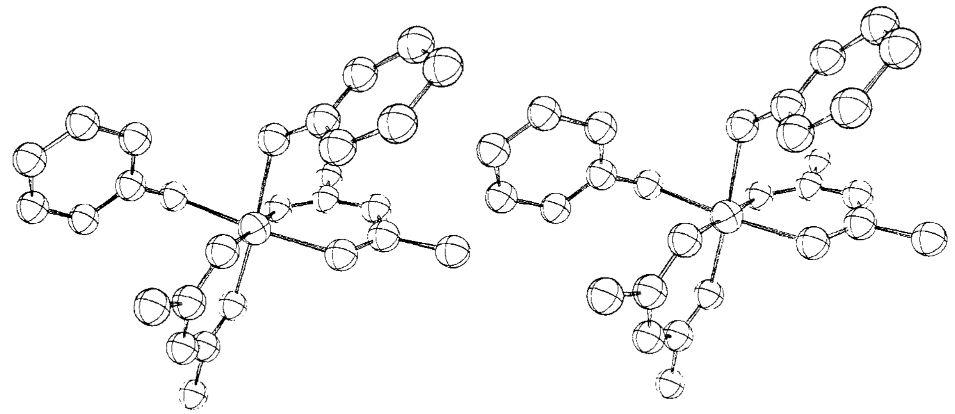

Figure 2.—Stereoscopic pair of $Ni(AA)_2(C_5H_5NO)_2$ molecules. The labeling of the atoms may be determined by a comparison with Figure 1.

Table I gives the final observed and calculated structure factors. On the final full-matrix least-squares cycle the largest variation of a heavy-atom positional parameter was 0.0006 while the largest temperature factor shift was 0.1; in all cases the shifts were smaller than the estimated standard deviations. The final heavy-atom parameters are given in Table II.

Description and Discussion of the Structure

The crystal is composed of discrete molecules, $Ni(AA)_2(C_5H_5NO)_2$, in which the six oxygens are coordinated to the nickel in a very nearly regular octahedral array. The bond distances and angles internal to these molecules are indicated in Table III. In Figure 1 the over-all molecular geometry is illustrated along with the atom labeling, and average values of chemically equivalent bond distances are given. A pair of stereoscopic representations is provided in Figure 2 to permit the reader to appreciate the details of the geometry. The closest Ni–Ni approach is 6.882 Å which occurs within the unit cell for molecules related by x, y, z and $^1/_2 - x$, $^1/_2 - y$, $-z$. This juxtaposition is achieved by efficient molecular packing and no specific intermolecular interactions are indicated.

The two pyridine N-oxide molecules occupy positions *cis* to one another in the coordination sphere of the nickel. This contrasts with the solid-state structures of $M(AA)_2(H_2O)_2$[8,9] and $M(AA)_2(C_5H_5N)_2$[10] (M = Co, Ni), in which the neutral monodentate ligands occupy *trans* positions. However, precedents for a *cis*-coordination geometry in divalent metal acetylacetonate compounds are provided by the crystal structures of $[Ni(AA)_2]_3$,[15] $[Co(AA)_2]_4$,[16] and $[Co(AA)_2H_2O]_2$.[17] These polymeric complexes involve a *cis*-octahedral arrangement of the terminal chelate rings. Also, complex anions of the type $M(AA)_3^-$ [18–22] necessarily involve coordination of this sort. These findings, taken together, suggest that there is very little energy difference between *cis* and *trans* structures of this type. Crystal-packing forces may very well determine the solid-state conformation in any particular example. The problem of the structures of $M(AA)_2L_2$ complexes in solution is of course not solved, but the present results suggest that the possibility of a *cis* structure in solution should not be ignored. For $Ni(AA)_2(C_5H_5N)_2$ in solution, Hashagen and Fackler[10] averred that their electronic spectral data were consistent with a *trans* structure, but their data do not rule out a *cis* configuration, or, what is even more likely, an equilibrium mixture of the two forms. Complexes of this type are quite

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(15) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

(16) F. A. Cotton and R. C. Elder, *ibid.*, **4**, 1145 (1965).

(17) F. A. Cotton and R. C. Elder, *ibid.*, **5**, 423 (1966).

(18) F. P. Dwyer and A. M. Sargeson, *J. Proc. Roy. Soc. N. S. Wales*, **90**, 29 (1956).

(19) M. Peter, *Phys. Rev.*, **116**, 1432 (1959).

(20) W. H. Watson, Jr., and C.-T. Liu, *Inorg. Chem.*, **5**, 1074 (1966).

(21) W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchison, and G. N. La Mar, *J. Am. Chem. Soc.*, **88**, 2436 (1966).

(22) B. Granoff, Ph.D. Thesis, Princeton University, 1966.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×3) FOR $Ni(AA)_2(C_5H_5NO)_2$[a]

H,K	L	FOB	FCA
0, 0	2	728	807
	4	60	62
	6	136	134
	8	12	-31
	10	64	-68
	12	149	-154
	14	154	-171
	16	124	-123
	18	10	-9
	20	14	7
0, 2	0	514	547
	1	164	171
	2	186	176
	3	45	-42
	4	104	-101
	5	250	-234
	6	237	-235
	7	2	5
	8	61	-66
	9	13	-20
	10	37	-40
	11	46	-42
	12	74	-64
	13	21	-26
	14	79	-80
	15	119	-123
	16	63	-56
	17	99	-99
	18	20	20
	19	13	-20
	20	26	29
0, 4	0	153	-153
	1	17	19
	2	128	-125
	3	206	215
	4	171	165
	5	261	281
	6	151	-136
	7	312	310
	8	77	-75
	9	204	206
	10	70	65
	11	39	44
	12	0	-6
	13	28	-18
	14	20	-23
	15	88	-81
	16	31	-26
	17	61	-59
	18	20	13
	19	43	-40
0, 6	0	94	-95
	1	38	40
	2	112	-119
	3	118	123
	4	113	-113
	5	270	271
	6	29	-25
	7	279	277
	8	80	83
	9	109	106
	10	64	61
	11	9	-12
	12	57	53
	13	9	-4
	14	17	-19
	15	45	-44
	16	0	-14
	17	53	-46
	18	25	19
	19	30	-27
0, 8	0	84	-84
	1	67	65
	2	80	-84
	3	112	111
	4	23	-26
	5	79	81
	6	14	-17
	7	53	51
	8	114	114
	9	8	1
	10	110	109
	11	20	-27
	12	25	25
	13	10	-2
	14	22	21
	15	54	-55
	16	25	13
	17	36	-40
	18	21	-17
0, 10	0	312	-312
	1	25	29
	2	167	-162
	3	4	6
	4	52	-51
	5	14	-10
	6	39	-36
	7	41	-43
	8	13	16
	9	27	33
	10	8	-8
	11	52	44
	12	60	60
	13	20	-11
	14	62	66
	15	10	2
	16	19	23
	17	21	14
0, 12	0	81	-78
	1	19	-11
	2	73	-74
	3	79	-78
	4	37	36
	5	60	-53
	6	95	99
	7	27	27
	8	28	35
	9	65	66
	10	8	-5
	11	26	35
	12	27	33
	13	45	54
	14	28	32
	15	75	86
0, 14	0	49	-49
	1	13	-2
	2	9	4
	3	87	-85
	4	27	36
	5	54	-56
	6	30	35
	7	41	-36
	8	60	70
	9	63	-57
	10	15	17
	11	17	-26
	12	10	-7
	13	16	15
0, 16	0	10	-6
	1	16	-9
	2	0	9
	3	6	-13
	4	17	24
	5	11	-11
	6	0	-10
	7	77	-63
	8	18	-12
	9	49	-51
	10	20	-17
0, 18	0	19	23
	1	18	11
	2	15	13
	3	0	4
	4	18	15
	5	9	2
	6	9	-11
1, 1	-20	11	1
	-19	0	-11
	-18	56	55
	-17	10	12
	-16	85	82
	-15	36	36
	-14	93	97
	-13	38	38
	-12	59	65
	-11	0	-4
	-10	152	136
	-9	26	-34
	-8	45	34
	-7	235	-228
	7	90	90
	8	103	109
	9	86	69
	10	15	7
	11	72	73
	12	11	-1
	13	16	16
	14	89	-90
	15	18	-20
	16	121	-114
	17	0	-15
	18	42	-42
	19	2	1
1, 3	-20	5	14
	-19	21	-31
	-18	46	44
	-17	28	26
	-16	9	9
	-15	78	75
	-14	15	7
	-13	118	117
	-12	44	-49
	-11	202	208
	-10	49	-58
	-9	85	88
	1	420	-420
	9	72	79
	10	58	55
	11	65	56
	12	56	51
	13	16	-12
	14	70	-67
	15	73	-69
	16	65	-59
	17	36	-44
	18	14	-22
	19	19	-16
1, 5	-19	20	-22
	-18	19	26
	-17	40	29
	-16	0	2
	-15	4	8
	-14	9	8
	-13	76	71
	-12	0	3
	-11	126	123
	-10	3	-5
	-9	19	27
	-8	64	-62
	-7	46	54
	-6	25	-21
	-5	16	29
	-4	40	-41
	-3	23	-33
	-2	94	-97
	-1	272	-291
	0	115	113
	1	200	-213
	2	96	-99
	3	194	-198
	4	113	-118
	5	0	-6
	6	73	-68
	7	247	243
	8	17	-15
	9	74	75
	10	25	-30
	11	60	62
	12	12	9
	13	16	25
	14	8	-13
	15	31	-27
	16	18	-13
	17	16	10
	18	21	16
	19	30	-32
1, 7	-19	21	-13
	-18	37	-35
	-17	26	23
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	-9	27	-24
	-8	43	-44
	-7	115	-116
	-6	0	-6
	-5	115	-118
	-4	37	39
	-3	48	-39
	-2	8	16
	-1	39	-39
	0	0	9
	1	41	-37
	2	36	-42
	3	10	-20
	4	28	26
	5	57	50
	6	47	60
	7	76	75
	8	14	8
	9	52	55
	10	8	11
7, 15	-10	0	-3
	-9	0	-7
	-8	29	35
	-7	31	-31
	-6	0	12
	-5	37	-29
	-4	0	-8
	-3	53	-48
	-2	23	-14
	-1	30	-26
	0	31	-27
	1	19	27
	2	50	-48
	3	41	34
	4	16	-19
	5	46	42
	6	14	14
	7	43	48
7, 17	-4	0	-6
	-3	30	-24
	-2	48	-49
	-1	18	-15
	0	52	-52
	1	27	29
8, 0	-18	101	-92
	-16	45	-47
	-14	25	-26
	-12	55	-51
	-10	144	145
	-8	239	238
	-6	177	165
	-4	365	339
	-2	178	155
	0	53	-58
	2	0	22
	4	69	-51
	6	203	-191
	8	141	-131
	10	32	-40
	12	41	30
	14	9	13
8, 2	-19	26	28
	-18	45	-45
	-17	42	-38
	-16	56	-55
	-15	0	-20
	-14	35	-49
	-13	51	51
	-12	21	-16
	-11	66	-62
	-10	22	14
	-9	106	-110
	-8	97	105
	-7	92	-67
	-6	103	115
	-5	75	-63
	-4	122	112
	-3	81	89
	-2	78	79
	-1	105	110
	0	27	-32
	1	40	55
	2	23	-24
	3	32	29
	4	61	-62
	5	19	9
	6	134	-128
	7	7	-17
	8	60	-56
	9	0	22
	10	38	-34
	11	0	-14
	12	46	43
	13	62	-56
	14	47	53
	15	32	-34
8, 4	-19	15	15
	-18	12	8
	-17	15	-12
	-16	24	-18
	-15	47	-50
	-14	17	7
	-13	28	-28
	-12	0	-2
	-11	79	-74
	-10	5	7
	-9	98	-95
	-8	6	24
	-7	59	-58
	-6	66	65
	-5	43	42
	-4	67	59
	-3	210	202
	-2	14	-10
	-1	299	280
	0	70	70
	1	234	219
	2	0	-7
	3	41	36
	4	13	-13
	5	12	21
	6	0	-3
	7	27	29
	8	5	-5
	9	0	19
	10	22	-31
	11	49	-45
	12	19	-12
	13	76	-74
	14	13	13
	15	21	-30
8, 6	-18	24	24
	-17	15	3
	-16	45	54
	-15	34	-39
	-14	45	43
	-13	34	-31
	-12	8	-4
	-11	70	-71
	-10	18	-14
	-9	43	-34
	-8	28	-27
	-7	48	-46
	-6	16	-19
	-5	0	-13
	-4	36	-38
	-3	195	198
	-2	89	-67
	-1	230	240
	0	52	-49
	1	169	159
	2	15	-11
	3	21	16
	4	20	18
	5	0	-2
	6	0	-20
	7	2	-22
	8	16	15
	9	29	-19
	10	21	-30
	11	63	-65
	12	23	-29
	13	86	-90
	14	20	-18
8, 8	-17	22	-32
	-16	45	49
	-15	32	-42
	-14	56	59
	-13	13	-18
	-12	14	-12
	-11	26	-23
	-10	44	-42
	-9	25	-21
	-8	50	-47
	-7	54	-61
	-6	34	-27
	-5	0	-7
	-4	83	-74
	-2	96	-101
	-1	86	93
	0	36	46
	1	13	13
	2	20	10
	3	0	-12
	4	45	46
	5	23	-27
	6	41	31
	7	38	-42
	8	0	-4
	9	0	-0
	10	16	-17
	11	26	-24
	12	21	-28
	13	45	-45
8, 10	-16	23	17
	-15	27	-28
	-14	0	18
	-13	8	-6
	-12	3	-4
	-11	0	-2
	-10	17	-27
	-9	28	-32
	-8	42	-43
	-7	66	-76
	-6	88	-75
	-5	46	-48
	-4	128	-119
	-3	0	2
	-2	64	-65
	-1	35	-27
	0	0	2
	1	45	-32
	2	0	-9
	3	65	-58
	4	87	91
	5	0	-7
	6	72	69
	7	34	28
	8	56	52
	9	31	30
	10	13	28
	11	18	15
	12	0	8
8, 12	-14	0	-2
	-13	26	24
	-12	21	-19
	-11	27	20
	-10	19	8
	-9	30	21
	-8	34	-39
	-7	0	8
	-6	49	-50
	-5	36	-51
	-4	14	11
	-3	34	-43
	-2	0	7
	-1	12	15
	0	29	25
	1	18	-10
	2	37	26
	3	12	-21
	4	93	94
	5	49	44
	6	79	76
	7	54	61
	8	31	31
	9	51	53
	10	0	12
8, 14	-11	35	34
	-10	13	-16
	-9	34	40
	-8	21	-23
	-7	23	24
	-6	13	19
	-5	29	-18
	-4	0	8
	-3	38	-35
	-2	19	-17
	-1	53	-50
	0	15	-13
	1	41	-43
	2	25	-25
	3	33	-31
	4	9	13
	5	20	-15
	6	8	13
	7	2	4
8, 16	-6	29	22
	-5	22	29
	-4	16	12
	-3	23	-21
	-2	0	-10
	-1	40	-49
	0	17	-12
	1	17	-16
	2	21	-30
	3	12	7

[a] The signs of F_o apply to the real part of the structure factor.

labile and exchange their monodentate ligands rapidly with excess ligand molecules present in solution.[6,7] Thus a facile mechanism for converting between *cis* and *trans* forms is readily available through ligand exchange, although an isomerization mechanism without bond rupture is also quite possible. Complexes of the type $Ti(AA)_2X_2$ (X = halogen) have been shown to exhibit a *cis*-octahedral structure in solution;[23,24] however, the higher oxidation state and negatively charged monodenate ligands make the analogy with the present system inexact. Kluiber and Horrocks,[6] in their analysis of isotropic dipolar pmr shifts in solutions of paramagnetic complexes of the type $M(AA)_2(C_5H_5NO)_2$ (M = Co, Ni), assumed a *trans* structure in solution and, on the basis of this, determined that pyridine N-oxide and certain of its derivatives coordinate in an angular fashion with an M–O–N angle in the range 115–130°. While this angular mode of coordination is substantiated for the solid state by the present results (*vide infra*), the use of a *trans* model is called to question. The answer to the problem as to which form is present or predominates in solution must await further studies.

The nickel to ligand atom distances appear normal. The average nickel to acetylacetonate oxygen distance found here (2.02 Å) is in excellent agreement with those found for *trans*-$Ni(AA)_2(H_2O)_2$ (2.02 Å)[9] and for the terminal chelate oxygens of $[Ni(AA)_2]_3$ (2.01 Å).[15] The average distance from the nickel to the pyridine N-oxide oxygen found here is 2.10 Å. This is slightly, but perhaps significantly, shorter than the nickel to

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(23) R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Letters*, **3**, 117 (1967).

(24) D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965).

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Ni(AA)_2(C_5H_5NO)_2$[a]

Atom[b]	*x*	*y*	*z*	*B*, Å^2
Ni	0.2180 (1)	0.0537 (1)	−0.0443 (1)	*c*
O(1)	0.2769 (3)	−0.0262 (2)	0.0311 (2)	3.3 (1)
O(2)	0.1454 (3)	−0.0321 (2)	−0.1040 (2)	3.4 (1)
C(1)	0.2933 (11)	−0.1409 (6)	0.1043 (6)	5.0 (2)
C(2)	0.2517 (5)	−0.0987 (4)	0.0340 (4)	3.3 (1)
C(3)	0.1900 (6)	−0.1354 (4)	−0.0208 (4)	3.4 (2)
C(4)	0.1417 (5)	−0.1037 (4)	−0.0856 (4)	3.7 (1)
C(5)	0.0766 (9)	−0.1547 (6)	−0.1392 (7)	5.2 (2)
O(3)	0.3239 (4)	0.0460 (2)	−0.1017 (2)	4.1 (1)
O(4)	0.1535 (3)	−0.1340 (2)	−0.1184 (2)	3.3 (1)
C(6)	0.4329 (11)	0.0913 (9)	−0.1724 (8)	9.1 (3)
C(7)	0.3399 (7)	0.0997 (5)	−0.1457 (4)	5.2 (2)
C(8)	0.2837 (8)	0.1616 (5)	−0.1725 (5)	4.6 (2)
C(9)	0.1946 (6)	0.1740 (4)	−0.1602 (4)	3.7 (1)
C(10)	0.1391 (10)	0.2433 (6)	−0.1991 (5)	5.3 (2)
O(5)	0.1104 (3)	0.0723 (2)	0.0155 (2)	3.2 (1)
N(1)	0.1198 (4)	0.0447 (3)	0.0848 (3)	2.9 (1)
C(11)	0.0668 (6)	−0.0142 (4)	0.0997 (4)	3.4 (2)
C(12)	0.0730 (7)	−0.0408 (4)	0.1712 (4)	4.0 (2)
C(13)	0.1344 (7)	−0.0098 (5)	0.2262 (5)	4.8 (2)
C(14)	0.1918 (7)	0.0476 (5)	0.2111 (5)	5.2 (2)
C(15)	0.1851 (7)	0.0754 (5)	0.1387 (5)	4.5 (2)
O(6)	0.2851 (4)	0.1457 (2)	0.0199 (2)	3.7 (1)
N(2)	0.3754 (5)	0.1582 (3)	0.0272 (3)	3.1 (1)
C(16)	0.4022 (7)	0.2318 (4)	0.0176 (4)	3.7 (2)
C(17)	0.4955 (9)	0.2487 (6)	0.0314 (5)	5.2 (2)
C(18)	0.5628 (9)	0.1919 (6)	0.0480 (6)	5.6 (3)
C(19)	0.5305 (12)	0.1144 (7)	0.0570 (7)	5.5 (3)
C(20)	0.4379 (9)	0.0996 (5)	0.0466 (5)	4.4 (2)

[a] Standard deviations indicated in parentheses refer to the least significant digit(s). [b] Atoms labeled as in Figure 1. [c] Components of the anisotropic thermal tensor for Ni defined as in the text are: $B_{11} = 5.30\ (10)$, $B_{22} = 4.30\ (5)$, $B_{33} = 4.62\ (5)$, $B_{12} = -0.17\ (5)$, $B_{13} = 1.13\ (5)$, $B_{23} = 0.24\ (4)$.

TABLE III

BOND DISTANCES AND ANGLES OF $Ni(AA)_2(C_5H_5NO)_2$[a]

Distances, Å

Ni–O(1)	2.013 (4)	C(8)–C(9)	1.382 (14)
Ni–O(2)	2.004 (4)	C(9)–C(10)	1.527 (14)
Ni–O(3)	2.035 (5)	O(5)–N(1)	1.337 (6)
Ni–O(4)	2.029 (5)	N(1)–C(11)	1.326 (9)
Ni–O(5)	2.105 (5)	C(11)–C(12)	1.373 (11)
Ni–O(6)	2.088 (5)	C(12)–C(13)	1.328 (13)
O(1)–C(2)	1.289 (8)	C(13)–C(14)	1.349 (13)
O(2)–C(4)	1.265 (8)	C(14)–C(15)	1.396 (12)
C(1)–C(2)	1.502 (13)	C(15)–N(1)	1.346 (10)
C(2)–C(3)	1.370 (10)	O(6)–N(2)	1.321 (9)
C(3)–C(4)	1.375 (10)	N(2)–C(16)	1.331 (9)
C(4)–C(5)	1.510 (14)	C(16)–C(17)	1.375 (16)
O(3)–C(7)	1.269 (9)	C(17)–C(18)	1.373 (16)
O(4)–C(9)	1.258 (9)	C(18)–C(19)	1.418 (17)
C(6)–C(7)	1.537 (18)	C(19)–C(20)	1.359 (21)
C(7)–C(8)	1.368 (13)	C(20)–N(2)	1.354 (12)

Angles, Deg

O(1)–Ni–O(2)	90.2 (2)	O(3)–C(7)–C(8)	127.6 (9)
O(3)–Ni–O(4)	90.1 (2)	C(6)–C(7)–C(8)	117.9 (9)
O(2)–Ni–O(4)	89.4 (2)	C(7)–C(8)–C(9)	125.6 (8)
O(5)–Ni–O(6)	85.0 (2)	O(4)–C(9)–C(8)	126.2 (7)
O(1)–Ni–O(3)	92.4 (2)	O(4)–C(9)–C(10)	115.2 (8)
O(1)–Ni–O(5)	90.5 (2)	C(8)–C(9)–C(10)	118.6 (8)
O(1)–Ni–O(6)	91.1 (2)	Ni–O(5)–N(1)	119.2 (4)
O(2)–Ni–O(3)	92.8 (2)	O(5)–N(1)–C(11)	120.0 (6)
O(2)–Ni–O(5)	91.2 (2)	O(5)–N(1)–C(15)	119.8 (6)
O(4)–Ni–O(5)	87.0 (2)	C(11)–N(1)–C(15)	120.2 (6)
O(4)–Ni–O(6)	89.3 (2)	N(1)–C(11)–C(12)	120.5 (7)
O(3)–Ni–O(6)	90.8 (2)	C(11)–C(12)–C(13)	120.7 (8)
Ni–O(1)–C(2)	125.5 (4)	C(12)–C(13)–C(14)	119.3 (8)
Ni–O(2)–C(4)	126.6 (4)	C(13)–C(14)–C(15)	120.3 (9)
O(1)–C(2)–C(1)	114.6 (7)	N(1)–C(15)–C(14)	118.8 (8)
O(1)–C(2)–C(3)	124.1 (6)	Ni–O(6)–N(2)	122.4 (4)
C(1)–C(2)–C(3)	121.3 (7)	O(6)–N(2)–C(16)	116.9 (6)
C(2)–C(3)–C(4)	128.2 (7)	O(6)–N(2)–C(20)	121.6 (7)
O(2)–C(4)–C(3)	124.6 (7)	C(16)–N(2)–C(20)	121.5 (8)
O(2)–C(4)–C(5)	115.4 (7)	N(2)–C(16)–C(17)	118.7 (8)
C(3)–C(4)–C(5)	120.0 (7)	C(16)–C(17)–C(18)	122.9 (10)
Ni–O(3)–C(7)	122.2 (5)	C(17)–C(18)–C(19)	115.9 (12)
Ni–O(4)–C(9)	123.7 (5)	C(18)–C(19)–C(20)	120.1 (12)
O(3)–C(7)–C(6)	114.5 (9)	N(2)–C(20)–C(19)	120.7 (9)

[a] Standard deviations indicated in parentheses refer to the least significant digit(s).

water oxygen distance of 2.14 Å in $Ni(AA)_2(H_2O)$.[9] This indicates that of the two neutral oxygen donor ligands, pyridine N-oxide is the more strongly coordinating.

In the present structure the two independent pyridine N-oxide molecules containing O(5) and O(6) coordinate with Ni–O–N angles of 119.2 and 122.4°, respectively. This angular coordination is to be expected from a consideration of the directional properties of the lone-pair electrons on the oxygen which form the coordinate bond to the nickel. The angle of approximately 120° suggests that a reasonable description of the bonding in pyridine N-oxide involves sp^2 hybridization on the oxygen (two lone pairs and the N–O bond pair) with the third lone pair in a pure p orbital and available for $p\pi$–$p\pi$ interaction with the π system of the pyridine ring. If this π interaction were very important, one would expect the Ni–O–N plane and the plane of the pyridine ring to be coincident. The angles between the Ni–O–N planes and the least-squares planes of the pyridine rings for ligands containing O(5) and O(6) are 67.5 and 48.4°, respectively (The stereoscopic view, Figure 2, illustrates this twist well.) This suggests that π interaction of this sort is not of paramount importance in determining the configuration of the coordination. A description of the bonding in terms of a distortion from sp^3 hybridization on the oxygen is of course equally valid. The angular coordination is consistent with the apparent angular hydrogen bond found for the hydrochloride of the ligand.[25] Angular coordination has also been observed in phosphine oxide coordination compounds.[26,27]

The internal distances and angles of the pyridine N-oxide ligand, in particular the average N–O bond distance of 1.33 Å, agree well with those recently reported[4] for the bridging ligand in $[CuCl_2(C_5H_5NO)]_2$. The present N–O bond distance is 0.05 Å shorter than that found in the hydrochloride,[25] but, considering the probable uncertainty of that determination, no conclusions can be drawn from this difference. Tsoucaris[25] estimated that the N–O linkage in $C_5H_5NO{\cdot}HCl$ had ~20% π character. While the literature data[28,29] available on N–O bond lengths do not permit as smooth a plot of bond lengths *vs.* bond order to be drawn as was obtained by Cotton and Wing[30] for the C–O bond, a reasonable curve of similar character can be con-

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(25) G. Tsoucaris, *Acta Cryst.*, **14**, 914 (1961).

(26) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

(27) C-I. Brändén and I. Lindqvist, *Acta Chem. Scand.*, **15**, 167 (1961); **17**, 353 (1963).

(28) "Interatomic Distances, Supplement 1956–1959," Special Publication No. 11, The Chemical Society, London, 1965.

(29) A. Caron, G. J. Palenik, E. Goldish, and J. Donohue, *Acta Cryst.*, **17**, 102 (1964), and references therein.

(30) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).

structed. The N–O bond length for coordinated pyridine N-oxide (1.33 Å) falls in the steep portion of the curve where bond order is relatively insensitive to bond length but suggests that the π-bond character is small, of the order of 10–20%. This conclusion is consistent with the observed sizable twist of the pyridine rings out of the Ni–O–N planes. A further useful comparison is with the N–O bond length of 1.39 Å[29] in the aliphatic amine N-oxide, $(CH_3)_3NO$, where π bonding is impossible and the effect of charge separation[29] should roughly correspond to the present case. The pyridine N-oxide oxygens O(5) and O(6) are, respectively, 0.06 and 0.07 Å out of the least-squares planes through the pyridine rings. Similar deviations from planarity have been found for the N-oxide moiety in $C_5H_5NO \cdot HCl$[25] and $[CuCl_2(C_5H_5NO)]_2$.[4]

The bond lengths and angles of the acylacetonate chelate rings appear normal and compare well with those in the literature. The methyl carbons fall within 0.15 Å of the least-squares planes defined by the oxygens and carbons 2, 3, and 4 of the chelate rings. As has been noted in other acetylacetonate complexes,[9] the central metal does not lie exactly in the plane of the chelate ring. In the present structure the nickel atom falls 0.17 and 0.64 Å from the least-squares planes of chelate rings O(1)–C(2)–C(3)–C(4)–O(2) and O(3)–C(7)–C(8)–C(9)–O(4), respectively.

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CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY AND MATERIAL RESEARCH LABORATORY,
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The Crystal and Molecular Structure of Orthorhombic Vanadyl(IV) Pyridine-2,6-dicarboxylate Tetrahydrate[1]

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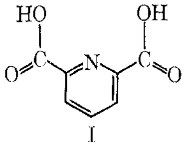
Optical spectra of polycrystalline vanadyl(IV) pyridine-2,6-dicarboxylate tetrahydrate (vanadyl(IV) 2,6-lutidinate tetrahydrate) have some interesting similarities to those of the low-symmetry vanadyl(IV) α-hydroxycarboxylates. The crystal structure of one form of vanadyl(IV) 2,6-lutidinate tetrahydrate has been determined to examine the effective symmetry of the chelate species involved and to obtain other structural information required to interpret the spectra of oriented crystals. The emerald green prismatic crystals are orthorhombic with $a = 8.68$, $b = 12.43$, and $c = 10.75$ Å. The space group is Pbcn and there are four units of $VOC_7H_3O_4N \cdot 4H_2O$ in the unit cell; $\rho_{\text{measd}} = 1.73$ g/cm³, $\rho_{\text{calcd}} = 1.733$ g/cm³; each molecule has C_2 symmetry. Three-dimensional intensity data were collected on multiple-film packs using the equiinclination Weissenberg technique. The structure was determined by Fourier methods and the positional and anisotropic thermal parameters were refined by least-squares methods to a final conventional *R* factor of 0.10 on 544 observed reflections. The vanadium atom is six-coordinated in a distorted octahedral site which closely approximates C_{2v} symmetry; one of the coordination positions is occupied by the vanadyl oxygen atom, two others are occupied by water molecules, and the remaining three, by the 2,6-lutidinate dianion acting as a tridentate ligand. The remaining two water molecules link the chelate molecules $(VOC_7H_3O_4N \cdot 2H_2O)$ by hydrogen bonding.

Introduction

There has been much interest in the very low-symmetry α-hydroxycarboxylate complexes with VO^{2+} since they exhibit four-band visible spectra[2] as opposed to the usual two or three strong bands observed in most vanadyl(IV) complexes. The Nujol mull spectrum (shown in Figure 1) of vanadyl(IV) complexed with pyridine-2,6-dicarboxylic acid (I) (hereafter referred to as 2,6-lutidinic acid)[3] reveals four bands similar to those of the low-symmetry α-hydroxycarboxylate species. We anticipated that the symmetry of the vanadyl(IV) 2,6-lutidinate complex might prove to be intermediate between that of ammonium vanadyl(IV) *d*-tartrate[4] which, from a spectroscopic examination, appears to be typical of low-symmetry vanadyl α-hydroxycarboxylate structures and the more usual case of approximately square-pyramidal local symmetry for vanadium in vanadyl structures.[5]


I

Difficulty in interpreting the spectra of the low-symmetry α-hydroxycarboxylates arises from the question-

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[1] Supported by ARPA Contract SD-131 through the Materials Research Laboratory at the University of Illinois and USPH GM 12470-03.

[2] J. Selbin and L. Murpurgo, *J. Inorg. Nucl. Chem.*, **27**, 673 (1965).

[3] The preparation of different hydrates of the potentially tridentate donor 2,6-lutidinic acid complexed with vanadyl(IV) has been reported by R. L. Dutta, S. Ghosh, and S. Lahiry, *Sci. Cult.* (Calcutta), **30**, 551 (1964).

[4] J. G. Forrest and C. K. Prout, *J. Chem. Soc.*, *A*, 1312 (1967).

[5] See, *e.g.*, R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **7**, 356 (1968).