conclusive proof since they give an indication of the "true" molecular symmetry and not just the effective symmetry determined by considering the ligand atoms as point charges. The latter approach has been used for the interpretation of absorption spectra with apparent success in cases where the actual number of components cannot be seen. In some of these cases the splittings were revealed from ORD or CD data.[2]

The Crystal and Molecular Structure of Bis(acetylacetonato)nickel(II)

BY G. J. BULLEN,[1a] R. MASON,[1b] AND PETER PAULING[1c]

A three-dimensional analysis of the crystal structure of bis(acetylacetonato)nickel(II) has established that the molecule is trimeric with octahedral coordination of each nickel ion. The Ni–Ni distances are 2.882 and 2.896 Å. (e.s.d. 0.018 Å.), the Ni–O bond lengths being of two main types and averaging 2.12 and 2.01 Å., respectively (e.s.d. 0.07 Å.). Data indicating that the structure is typical of a variety of nominally four-coordinate metal complexes are summarized while the crystal structure is discussed in relation to theories which appear to require some modification.

Experimental

Bis(acetylacetonato)nickel(II) was prepared by the reaction of nickel hydroxide (obtained from Analar nickel sulfate) with acetylacetone. The resulting blue-green hydrate was converted to the emerald-green anhydrous compound (m.p. 229–230°) by subliming it at 170–210° and a pressure of 0.2–0.4 mm., the water removed being absorbed on phosphorus pentoxide. There was a small amount of decomposition on sublimation, a brown residue being left. As bis(acetylacetonato)nickel(II) is easily hydrated and has a tendency to coordination by solvent molecules, recrystallization from solution was avoided, and crystals suitable for X-ray examination were prepared by slow sublimation under the conditions stated above. In this way well-shaped crystals up to 0.5 mm. long were prepared.

The crystals are orthorhombic, $a = 23.23 \pm 0.04$ Å., $b = 9.64 \pm 0.02$ Å., $c = 15.65 \pm 0.02$ Å.[2] The observed density (by flotation) is 1.455 ± 0.001 g./ml. (at 17°); the density calculated for 12 formula units $Ni(C_5H_7O_2)_2$ in the unit cell is 1.460 ± 0.008 g./ml. Systematic absences are: $(0kl)$ when l is odd and $(h0l)$ when h is odd, indicating space groups Pca2₁ or Pcam. Tests for pyroelectricity and piezoelectricity were negative, and a statistical survey of $(0kl)$ and $(h0l)$ intensities did not permit a conclusive choice between Pca2₁ and Pcam to be made. The subsequent analysis proved Pca2₁ to be correct. Forms well developed are {010}, {001}, {00$\bar{1}$}, {201}, {20$\bar{1}$}, and to a lesser degree {110}, the crystals appearing to be holohedral. Cleavage planes are (010) and (201). The crystals are optically positive with birefringence less than 0.008; the optic axis is approximately perpendicular to (201).

For intensity measurements, crystals were sealed in thin-walled soda glass tubes (approximately 0.03 mm. thick) to prevent hydration of the crystals by atmospheric moisture. Three-dimensional data were collected from two sets of oscillation photographs (5° oscillation ranges, overlapping by 2°) taken, using Cu Kα radiation, with a and c as oscillation axes. From these photographs the intensities of all $(0kl)$, $(h0l)$, and $(hk0)$ reflections present and of the stronger of the general (hkl) reflections were measured, 1073 in all. It is estimated that only those reflections with $|F|$ less than 16 (compared to the largest observed $|F| = 282$, for (010)) were neglected. The very strong intensities were measured from a short exposure rotation photograph, all intensities being estimated visually by comparison with a standard scale.

Crystals were sometimes found to decompose after being sealed. In these circumstances the use of oscillation photographs offered an advantage over the use of Weissenberg photographs, since they required comparatively short exposures (1 hr.) and any decomposition occurring would be soon detected. The linear absorption coefficient for Cu Kα is 24.7 cm.[-1]; crystals with their largest dimension equal to 0.5 mm. were used and no absorption corrections were made.

Intensities were corrected for Lorentz and polarization factors using the chart for oscillation photographs constructed by Kaan and Cole.[4] Corrections to intensities of upper layer reflections for variation in spot size and oblique incidence of the diffracted ray on the film were made and intensities put on an absolute scale using Wilson's method and later through the comparison of observed and calculated structure factors.

Analysis of the Structure

At the start of the analysis space groups Pca2₁ and Pcam both had to be considered as it had not been possible to choose between them from the systematic absences or by statistical tests. Attempts were made first to locate the 12 nickel atoms in the unit cell, possible arrangements of which are: (i) in Pca2₁, 3 sets of 4 in general position 4a, (ii) in Pcam, 1 set of 8 in general position 8e and 1 set of 4 in special positions (either 4a-$\bar{1}$, 4b-$\bar{1}$, 4c-2, 4d-m), or (iii) in Pcam, 3 sets of 4 all in special positions (chosen from 4a, b, c, or d).

The selection of the correct arrangement and the deduction of the nickel atom positions was made from the three-dimensional Patterson function employing, in particular, Patterson–Harker sections and lines. In the line $P(0, 0, W)$ there is, apart from the origin peak, only one small peak at $W = \frac{1}{2}$, there being a smooth drop from the origin along most of the length of the line. This suggests strongly that the space

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(2) Data were given in a previous publication[3] for a different orientation of the crystallographic axes. The space group P2₁ab used there has been here reoriented to Pca2₁, the standard crystallographic setting.

(3) G. J. Bullen, *Nature*, **177**, 537 (1956).

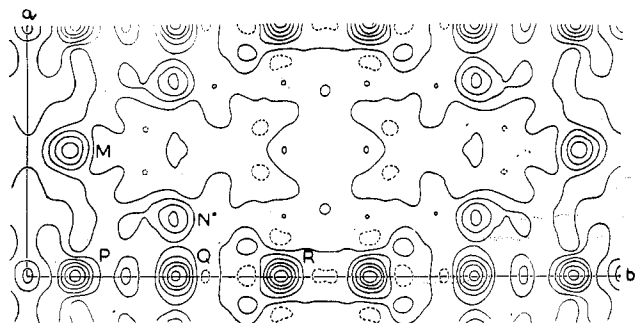(4) G. Kaan and W. F. Cole, *Acta Cryst.*, **2**, 38 (1949).

Figure 1.—The Harker–Patterson section P(U, V, $1/2$) for bis-(acetylacetonato)nickel(II).

group is Pca2$_1$ (arrangement (i)) since, if a mirror plane were present, there would be many vectors, parallel to W, between pairs of atoms related by mirror symmetry. The section P(U, V, $1/2$) should then show six major peaks, attributable to vectors between nickel atoms related by the screw axis and c glide plane. Of these (a) 3 will be of type $2x$, $2y$, $1/2$, for which vectors between atoms related by the 2_1 axis are responsible, and (b) 3 of type $1/2 - 2x$, 0, $1/2$, from vectors between atoms related by the c glide plane. Peaks P, Q, R in this section (Figure 1) were identified with group (b) and peaks, M, N, R with group (a); two of the six peaks coincide at R as a result of one nickel atom having a y coordinate close to 0. From the positions of these peaks, the following approximate coordinates for the three nickel atoms were deduced.

	x	y
Ni$_1$	0.04	0.25
Ni$_2$	0.12	0.12
Ni$_3$	0.21	0

The choice between these coordinates and others related by symmetry, which could equally well have satisfied the Patterson section, was made by examining the Patterson projection P($UV0$) for the sets of vectors between Ni$_1$ and Ni$_2$ and between Ni$_2$ and Ni$_3$. The projection P($UV0$) was chosen because it contains all the nickel–nickel vectors irrespective of their z coordinates, which were not known at this stage of the analysis. Since in Pca2$_1$ the position of the origin with respect to the symmetry elements in the z direction is arbitrary, the z coordinate of Ni$_2$ may be put equal to 0; the z coordinates for Ni$_1$ (0.092) and Ni$_3$ (-0.098) were deduced from the nickel–nickel vectors in the three-dimensional Patterson synthesis.

The distances, calculated from these approximate coordinates, between Ni$_1$ and Ni$_2$ and between Ni$_2$ and Ni$_3$ are about 2.8 Å., so that it is clear that the three nickels in the asymmetric unit, together with their associated acetylacetone groups, form one large molecule. This fact, and the consequent doubt as to whether the mode of arrangement of the chelate groups around the nickel atoms is tetrahedral or octahedral, has already been commented on.[3] Attempts were made to use the Fourier projections $\rho(XY0)$ and $\rho(X0Z)$, computed using the phases calculated from the nickel

atom coordinates only, to assign coordinates to the oxygen and carbon atoms for several likely trial arrangements, but they were not successful.

With the availability of large-scale computing facilities some 6 years later, it became possible to utilize the complete three-dimensional data. After two cycles of block-diagonal least-squares refinement of the nickel coordinates and anisotropic temperature factors, the Fourier synthesis $\rho(XYZ)$ was calculated; the clearly resolved oxygen atoms were found to lie in positions which indicated octahedral coordination of each nickel atom in the trimeric molecule. The nickel and oxygen atomic positions were again refined by a single least-squares analysis when the usual residual error factor comparing observed and calculated structure factor amplitudes was 0.35; bond lengths and angles of all the nickel–oxygen bonds were, at this stage, quite reasonable. A second Fourier synthesis based on these nickel and oxygen contributions now indicated the general arrangement of the acetylacetone rings; it was also realized that the molecule was virtually centrosymmetric in the lattice, a fact which was used to position four carbon atoms which were not clearly indicated in the Fourier map. Atomic coordinates were thus assigned to all thirty carbons, although after inspection of the calculated carbon–carbon and carbon–oxygen bond lengths some adjustments of the Fourier coordinates were made in order to bring these values into line with a more acceptable model. Inclusion of all nickel, oxygen, and carbon atoms reduced the residual R factor to 0.27, which in turn was reduced to the present value of 0.14 in twelve cycles of least-squares refinement. In this least-squares analysis unit weights for all observed reflections were used *faute de mieux*. The final atomic coordinates and temperature factor coefficients are listed in Table I together with their estimated standard deviations. A composite representation of the final electron density synthesis $\rho(XYZ)$ is shown in Figure 2. Observed and calculated structure factors are listed in Table II.

Discussion

The relatively large estimated standard deviations of the atomic coordinates obviously preclude any detailed discussion of the electron distribution in the complex in terms of the intramolecular bond lengths and angles; we feel justified therefore in quoting only the average dimensions of the acetylacetone ligand (Figure 3), although some features of the nickel–nickel and nickel–oxygen bond lengths (Figure 4) are worthy of comment. The really striking result of the analysis has, however, been its unequivocal determination of a slightly distorted octahedral coordination of all the nickel atoms in the trimer. This coordination results from the sharing of triangular faces of adjacent octahedra, an acetylacetonato oxygen being situated at each apex of the linear chain of fused octahedra. It is only in the trimer and in the infinite polymer that octahedral coordination can be achieved with a molecule, essentially of the form AB$_4$, in which all metal–ligand bonds

Table Ia

Bis(acetylacetonato)nickel(II): Atomic Coordinates

	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
Ni_1	0.03439	0.26078	0.10082	0.00039	0.00098	0.00097
Ni_2	0.12068	0.12216	−0.00030	0.00034	0.00105	0.00115
Ni_3	0.20733	−0.02331	−0.09866	0.00038	0.00096	0.00097
O_1	0.0340	0.1611	−0.0219	0.0015	0.0048	0.0033
O_2	0.1152	−0.0923	−0.0438	0.0017	0.0034	0.0036
O_3	0.2070	0.0855	0.0154	0.0013	0.0043	0.0036
O_4	0.1206	0.3209	0.0439	0.0015	0.0030	0.0039
O_5	0.0950	0.0958	0.1183	0.0012	0.0030	0.0031
O_6	0.1523	0.1535	−0.1149	0.0015	0.0033	0.0033
O_7	−0.0174	0.3973	0.0464	0.0014	0.0046	0.0042
O_8	0.0525	0.3520	0.2169	0.0020	0.0040	0.0032
O_9	0.2461	−0.1998	−0.0481	0.0020	0.0042	0.0040
O_{10}	0.1945	−0.0958	−0.2090	0.0014	0.0043	0.0033
O_{11}	−0.0329	0.1464	0.1434	0.0024	0.0055	0.0050
O_{12}	0.2774	0.0859	−0.1302	0.0016	0.0033	0.0046
C_1	0.0006	0.0566	−0.0553	0.0029	0.0080	0.0075
C_2	0.0815	−0.1164	−0.0870	0.0019	0.0049	0.0053
C_3	−0.0632	0.1187	−0.0618	0.0020	0.0079	0.0043
C_4	0.0887	−0.2688	−0.1115	0.0028	0.0050	0.0080
C_5	0.0184	−0.0944	−0.0821	0.0032	0.0105	0.0059
C_6	0.2386	0.2135	0.0642	0.0024	0.0088	0.0070
C_7	0.1730	0.3836	0.0288	0.0035	0.0043	0.0107
C_8	0.3097	0.1714	0.0045	0.0038	0.0058	0.0111
C_9	0.1498	0.5161	0.0942	0.0026	0.0095	0.0066
C_{10}	0.2198	0.3260	0.0881	0.0033	0.0086	0.0100
C_{11}	0.2800	0.2088	−0.1539	0.0027	0.0062	0.0041
C_{12}	0.1758	0.2954	−0.1466	0.0029	0.0091	0.0061
C_{13}	0.3437	0.2596	−0.1839	0.0029	0.0070	0.0073
C_{14}	0.1331	0.3656	−0.1921	0.0032	0.0055	0.0072
C_{15}	0.2215	0.2898	−0.2225	0.0028	0.0083	0.0095
C_{16}	0.0271	0.4752	0.2175	0.0023	0.0073	0.0056
C_{17}	−0.0332	0.5431	0.0711	0.0028	0.0084	0.0052
C_{18}	0.0296	0.5412	0.3281	0.0026	0.0062	0.0053
C_{19}	−0.0749	0.6222	0.0400	0.0032	0.0054	0.0098
C_{20}	−0.0167	0.5429	0.1730	0.0030	0.0053	0.0055
C_{21}	−0.0262	0.0393	0.1874	0.0030	0.0070	0.0058
C_{22}	0.0830	−0.0067	0.1616	0.0022	0.0073	0.0044
C_{23}	−0.0626	−0.0102	0.2295	0.0034	0.0058	0.0062
C_{24}	0.1347	−0.1078	0.1636	0.0032	0.0066	0.0060
C_{25}	0.0211	−0.0723	0.1882	0.0029	0.0065	0.0069
C_{26}	0.2123	−0.1920	−0.2521	0.0031	0.0060	0.0091
C_{27}	0.2681	−0.2734	−0.1013	0.0021	0.0077	0.0051
C_{28}	0.2057	−0.2554	−0.3247	0.0031	0.0068	0.0068
C_{29}	0.3073	−0.3582	−0.0610	0.0039	0.0075	0.0060
C_{30}	0.2517	−0.2949	−0.1888	0.0025	0.0056	0.0036

are equivalent[5]; that is an infinite polymer consisting of octahedra sharing opposite edges and the trimer of octahedra sharing opposite faces. Octahedral coordination of nickel was suspected when the Patterson synthesis had indicated the trimeric nature of the molecule but bis(acetylacetonato)nickel (Ni(acac)$_2$) has long been cited, on the basis of its magnetic properties, as a probable example of a tetrahedral Ni^{2+} complex.[6] It has more recently been realized, however, that no *a priori* correlation between magnetic moment and structure of these complexes is possible since the magnetic properties will depend critically on the symmetry and strength of the ligand field.   It has been shown[7,8] that the energy separation between the lowest singlet and triplet states may be large or comparable with kT

and indeed either may be the ground state. The magnetic moment of Ni(acac)$_2$ has been reported variously in the range 3.04–3.45 B.M., for example[9,10]; the average susceptibility, $\bar{\chi}$, follows a Curie–Weiss behavior with a Weiss constant of 4°.[11] This latter result is perhaps surprising in relation to the structure since it might have been thought that the trimeric arrangement would have afforded a good electronic framework for a superexchange process between nickel atoms utilizing the bridging oxygens. This phenomenon must be very restricted since part of the observed Weiss constant may originate from the ligand field distortion[12]; although the ground term in an octahedral complex of Ni^{2+} is the orbitally nondegenerate $^3A_2$, mixing-in of the higher T_2 terms could provide

(5) G. J. Bullen, R. Mason, and P. J. Pauling, *Nature*, **189**, 291 (1961).

(6) L. Pauling, "The Nature of the Chemical Bond," 1st Ed., Oxford University Press, 1940, p. 119.

(7) G. Maki, *J. Chem. Phys.*, **28**, 650; **29**, 162 (1958).

(8) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

(9) R. W. Asmussen, Thesis, Copenhagen, 1944.

(10) R. H. Holm, Ph.D. Thesis, Massachusetts Institute of Technology, 1959.

(11) A. Earnshaw, private communication (1962).

(12) B. N. Figgis, *Trans. Faraday Soc.*, **56**, 1553 (1960).

TABLE Ib

THE THERMAL VIBRATION COEFFICIENTS b_{ij} OF THE EXPRESSION FOR THE DEBYE FACTOR $B = 2^{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)}$

Ni$_1$	0.00136	0.00860	0.01010	−0.00438	0.00017	0.00265
Ni$_2$	0.00023	0.01219	0.01034	−0.00979	0.00113	−0.00005
Ni$_3$	0.00127	0.0088	0.00984	−0.00261	0.00421	−0.00038
O$_1$	0.00171	0.02551	0.0106	0.0147	0.0087	−0.0127
O$_2$	0.0031	0.0046	0.0153	−0.0032	0.0098	0.0084
O$_3$	0.0007	0.0190	0.0153	−0.0104	−0.0114	0.0014
O$_4$	0.0015	0.0015	0.0190	−0.0192	0.0110	0.0007
O$_5$	0.0004	0.0035	0.0103	−0.0107	−0.0051	0.0057
O$_6$	0.0018	0.0047	0.0104	−0.0022	−0.0054	−0.0054
O$_7$	0.0005	0.0215	0.0184	0.0105	0.0023	0.0103
O$_8$	0.0042	0.0091	0.0076	0.0029	−0.0018	0.0006
O$_9$	0.0023	0.0200	0.0146	−0.0130	0.0033	0.0049
O$_{10}$	0.0006	0.0182	0.0109	0.0076	0.0045	0.0030
O$_{11}$	0.0060	0.0363	0.0243	0.0317	0.0207	0.0285
O$_{12}$	0.0026	0.0026	0.0238	0.0009	0.0080	0.0038
C$_1$	0.0018	0.0374	0.0210	−0.0025	0.0004	−0.0014
C$_2$	0.0008	0.0052	0.0138	−0.0068	−0.0075	0.0060
C$_3$	0.0002	0.0325	0.0057	0.0070	0.0013	0.0037
C$_4$	0.0030	0.0024	0.0300	0.0060	−0.0065	0.0024
C$_5$	0.0031	0.0629	0.0105	−0.0205	−0.0064	0.0063
C$_6$	0.0014	0.0377	0.0238	−0.0069	−0.0155	−0.0083
C$_7$	0.0053	0.0080	0.0661	−0.0339	−0.0233	−0.0055
C$_8$	0.0063	0.0049	0.0653	0.0035	−0.0264	0.0093
C$_9$	0.0018	0.0363	0.0237	−0.0186	0.0177	−0.0043
C$_{10}$	0.0035	0.0226	0.0425	−0.0036	0.0079	−0.012
C$_{11}$	0.0033	0.0125	0.0175	0.0080	0.0079	−0.0121
C$_{12}$	0.0025	0.0379	0.0128	−0.0223	0.0016	−0.0057
C$_{13}$	0.0030	0.0146	0.0236	−0.0079	0.0081	−0.0099
C$_{14}$	0.0048	0.0025	0.0334	0.0070	−0.0175	0.0060
C$_{15}$	0.0024	0.0260	0.0383	0.0303	−0.0137	−0.0130
C$_{16}$	0.0013	0.0242	0.0207	−0.0237	0.0060	0.0128
C$_{17}$	0.0028	0.0377	0.0113	−0.0350	0.0127	−0.0141
C$_{18}$	0.0024	0.0134	0.0112	0.0219	−0.0028	0.0052
C$_{19}$	0.0045	0.0024	0.0420	−0.0037	−0.0130	0.0062
C$_{20}$	0.0044	0.0070	0.0133	0.0165	0.0014	−0.0058
C$_{21}$	0.0035	0.0186	0.0160	0.0347	0.0122	0.0009
C$_{22}$	0.0010	0.0172	0.0058	−0.0135	0.0041	−0.0003
C$_{23}$	0.0068	0.0028	0.0372	0.0103	0.0336	0.0114
C$_{24}$	0.0047	0.0107	0.0109	−0.0021	−0.0063	−0.0036
C$_{25}$	0.0034	0.0137	0.0187	0.0095	0.0061	−0.0100
C$_{26}$	0.0038	0.0065	0.0406	0.0064	0.0161	−0.0067
C$_{27}$	0.0005	0.0341	0.0094	−0.0161	−0.0043	0.0049
C$_{28}$	0.0042	0.013	0.0215	−0.0271	0.0063	−0.0111
C$_{29}$	0.0071	0.0161	0.0119	0.0035	−0.0080	−0.0069
C$_{30}$	0.0012	0.0195	0.0034	−0.0214	0.0077	−0.0101

some contribution to the slight deviations observed from a simple Curie law. The magnetochemical criterion of stereochemistry can, of course, be placed on a more certain basis if studies are made of the paramagnetic anisotropy of single crystals. Thus the anisotropy of Ni(acac)$_2$ should be quite small (∼30%) compared with that for a tetrahedral Ni^{2+} complex; as yet, however, we have not succeeded in growing crystals of the complex sufficiently large to carry out studies similar to those relating to tetrahedral Co^{2+} complexes.[13]

Our earlier suggestion[5] that "trimerization occurs with other complexes of this type if the chelate groups are not too bulky for steric hindrance to prevent the association" has since been strikingly confirmed. Cotton and Fackler[14] have studied the magnetism and spectral properties of bis(2,6-dimethyl-3,5-heptane-

diono)nickel(II) and bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II). The latter is red and diamagnetic and can reasonably be assumed to be a spin-paired planar complex, whereas the former is paramagnetic (μ_{eff} = 3.41 B.M. at 24°) and green in the crystalline state. Solutions may be red, the color being a function of temperature and concentration. The extent of monomer–trimer equilibrium in solution can therefore be determined from spectral data, and Cotton and Fackler suggest that the concept of configurational equilibria between diamagnetic planar and paramagnetic tetrahedral forms of a wide variety of nominally four-coordinate species is less preferable than one involving monomer–trimer equilibria. Holm and McKinney[15] have separately discussed association phenomena in complexes of Schiff bases, while Fackler and Cotton[16] have further reported that the temperature dependence of the visible absorption spectra of bis(2,6-

(13) B. N. Figgis, M. Gerloch, and R. Mason, *Proc. Roy. Soc.* (London), **A279**, 210 (1964).

(14) F. A. Cotton and J. P. Fackler, *J. Am. Chem. Soc.*, **83**, 2818 (1961).

(15) R. H. Holm and T. M. McKinney, *ibid.*, **82**, 5506 (1960).

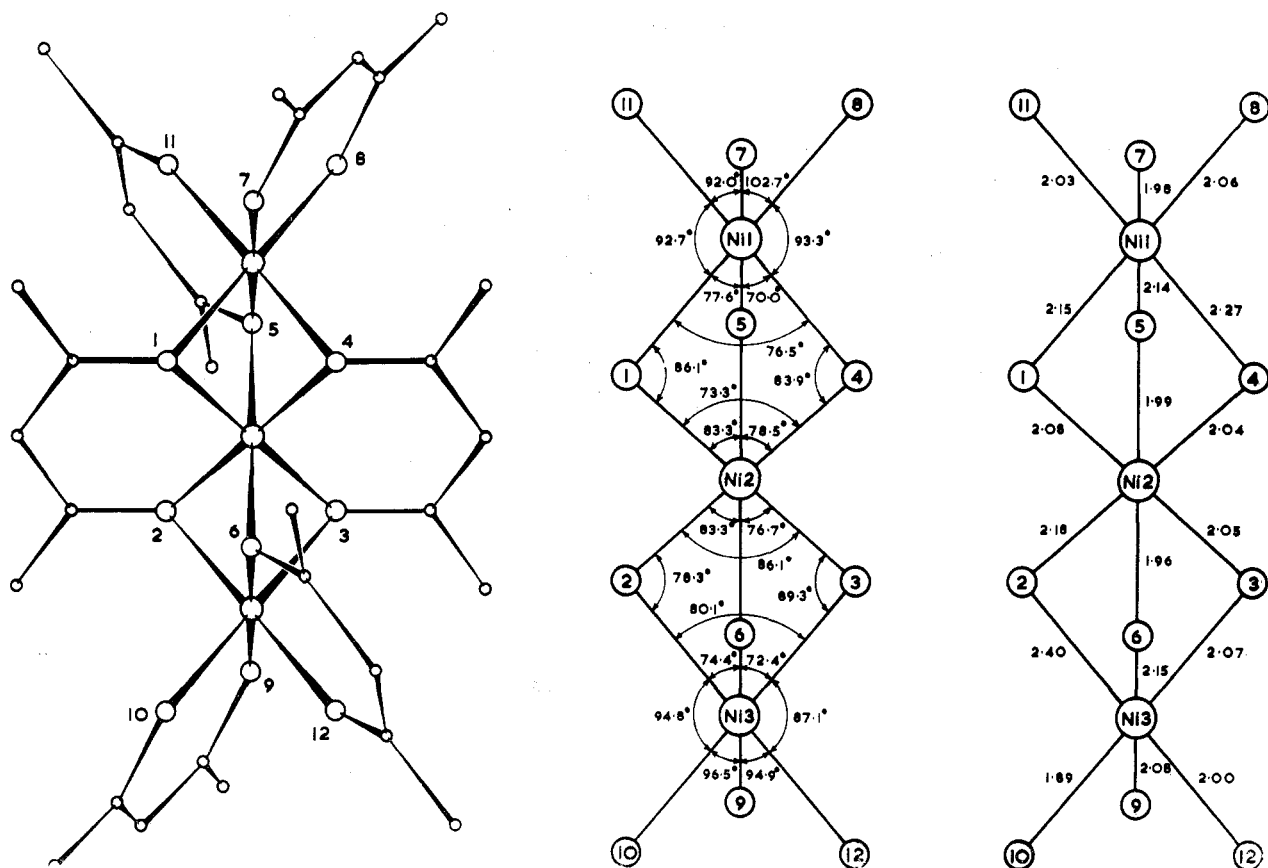(16) J. P. Fackler and F. A. Cotton, *ibid.*, **83**, 3775 (1961).

TABLE II

Figure 2.—Composite electron density synthesis of bis(acetylacetonato)nickel(II). Contours are drawn at 1 e Å.$^{-3}$ intervals, the zero contour being omitted.

Figure 3.—Average molecular dimensions of the coordinated acetylacetone ligands in bis(acetylacetonato)nickel(II): $\bar{\sigma}$ (C–O) = 0.08 Å.; $\bar{\sigma}$ (C–C) = 0.10 Å.

dimethyl-3,5-heptanediono)nickel(II),   bis(2,4-pentanediono)nickel(II),   and   bis(3-phenyl-2,4-pentanediono)nickel(II) dissolved in toluene is explicable in terms of a monomer–trimer equilibrium, the anhydrous complex together with bis(dibenzoylmethano)nickel(II) being isolated in both red and green forms. Graddon and Watton[17] showed that bis(acetylacetonato)nickel-(II) preserves its trimeric form in hydrocarbon solutions, Graddon[18] again showing that polymerization might be a common feature of apparent four-coordinated complexes. Bis(benzoylacetonato)nickel(II) and bis(acetylacetonato)cobalt(II) are both trimeric in nondonor solvents, while bis(acetylacetonato)oxo-

(17) D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961).

(18) D. P. Graddon, *ibid.*, **195**, 891 (1962).

Figure 4.—The molecular structure and Ni–Ni and Ni–O bond lengths and bond angles in bis(acetylacetonato)nickel(II).

vanadium(IV) is dimeric. It was claimed, however, that bis(acetylacetonato)zinc(II) is monomeric and tetrahedral, an explanation of the differences between the zinc and nickel complexes being given in terms of the zinc ion being unable to tolerate as large an effect of transferred charge as nickel(II), cobalt(II), and vanadium(IV). This argument is not conclusive and the data are somewhat inconsistent with our finding that in the solid state, at least, bis(acetylacetonato)-zinc may occur as trimers ($a = 19.2$ Å., $b = 8.4$ Å., $c = 24.4$ Å., $\beta = 113°$; with three formula units per asymmetric unit, $Z = 12$, $\rho_{calcd} = 1.45$ g./ml. compared with $\rho_{obsd} = 1.40 \pm 0.03$ g./ml.).

Steric hindrance between the alkyl groups of the ligand offers an explanation of the equilibrium constants determined by Cotton and Fackler.[14] On the basis of our earlier preliminary molecular dimensions, these authors calculated, from a model, that carbons to which the methyl groups are attached in adjacent acetylacetone rings have a separation of only 4.7 ± 0.2 Å. These carbon atoms and their separation are, in our nomenclature, C-1–C-22 (3.9 Å.), C-7–C-12 (3.6 Å.), C-2–C-21 (3.8 Å.), and C-6–C-11 (3.6 Å.); these contacts are comparable with the van der Waals diameter of the methyl group (4.0 Å.), so that increasing the size of the alkyl substituent of the ligand will lead to "overcrowding" and therefore to a tendency to dissociate the trimer.

In contrast to these data, which can be taken as conclusive evidence that the molecular structure of bis-

(acetylacetonato)nickel(II) is the same in solution as in the crystal, it has been suggested that the molecule is planar in the vapor phase.[19] The electron diffraction analysis is, however, quite inconclusive since the possibility of octahedral coordination was not explicitly considered; an approximate calculation of the radial distribution function of the present structure shows reasonable agreement with the observed data. These authors also suggest that the present crystal structure is that of a high-temperature modification; this is not the case nor, as was mentioned earlier, are the zinc and nickel bisacetylacetonates isomorphous as was reported by Shibata.[20]

In spite of the large estimated standard deviations, the nickel–oxygen bond lengths show a significant difference between those bonds in which the oxygen is bonded to only one nickel atom ($l = 2.01$ Å.) or shared between two nickel atoms ($l = 2.12$ Å.); the difference in bond lengths must be due, in part, to the change of atomic radius of oxygen following rehybridization. The bridging of the nickel atoms by oxygens O_1, O_2, O_3, O_4, O_5, and O_6 also leads to significant distortions from perfect octahedral symmetry of the ligand field surrounding the nickel ions; bond angles at the nickels range upward from 70°. The acetylacetonate ligands are arranged on a helix, the twelve oxygen atoms forming four equilateral triangles in parallel planes. Each triangle is rotated by 180° with respect to the preceding

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figure. The points of intersection of generalized helices with equidistant planes always form regular polygons in parallel planes with each polygon being rotated by a constant angle with respect to the preceding polygon.

An interesting feature of this structure is that the molecules are almost centrosymmetric[5] but are arranged in a noncentrosymmetric space group. This is, apparently, a rare situation; Herbstein and Schoening[21] were able to find only five examples of such an occurrence. Kitajgorodskij[22] maintains on the basis of his theory of close packing that it is impossible for centrosymmetric molecules to form a noncentrosymmetric structure. This view received support when van Nie-

kerk and Boonstra[23] showed that the molecules of 4,4'-dinitrodiphenyl (which had been one of the more reliable of the five examples of Herbstein and Schoening[21]) are in fact noncentrosymmetric in the crystal. They were inclined, from this discovery, to infer that possibly the remaining known exceptions to the rule would be found, on further study, to conform. However, the present work establishes the structure of bis(acetylacetonato)-nickel(II) as a definite exception to Kitajgorodskij's rule and therefore calls this rule to question.

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Equilibrium Studies of Uranyl Complexes. III. Interaction of Uranyl Ion with Citric Acid[1-3]

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A potentiometric study of complex formation between citric acid (H_3L) and the uranyl ion at 25° and ionic strengths of 0.1 and 1.0 (KNO_3) is reported. From the concentration dependence of the formation constant, it is concluded that polynuclear complexes are formed in which bridging between metal ions occurs through carboxylate and hydroxyl groups of the ligand. The values of the logarithms of the formation constant of the metal chelate $[UO_2L^-]/[UO_2^{2+}][L^{3-}]$ and of the dimerization constant $[(UO_2)_2L_2^{2-}]/[UO_2L^-]^2$ are found to be 7.40 and 4.07, respectively, at $\mu = 0.10$, and 6.87 and 3.96 at $\mu = 1.0$. Infrared absorption measurements of protonated and dissociated carboxyl groups in aqueous uranyl citrate system indicate the presence of both carboxylate and hydroxide bridging in the polynuclear complex. On the basis of the "core plus links" treatment of polynuclear complexes, the polymeric species in solution in the buffer region between 3 and $4^2/_3$ moles of base per mole of metal complex appears to be predominantly $(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_2^{16-}$.

Introduction

As a part of a general investigation of olation reactions of uranyl complexes,[4,5] a study of the nature of the uranyl citrate complexes formed in aqueous solutions and the conditions under which polynuclear complexes may be formed was undertaken. The probable formation of binuclear and ternuclear uranyl citrate chelates in the pH range 2–8 was reported by Feldman and co-workers[6,7] on the basis of polarographic, potentio-

metric, and spectrophotometric determinations. Subsequent potentiometric work by Feldman, *et al.*,[8] was given as confirmation of the original suggestion that a binuclear diolated uranyl citrate complex is formed at low pH and that a ternuclear species is formed as the pH is increased. A formation constant for the binuclear complex was reported. On the basis of nonequilibrium ultracentrifugation measurements of the 1:1 uranyl citrate system, Gustafson and Martell[9] have reported the formation of a dimer and a probable mixture of trimers and hexamers at 3 and $4^2/_3$ moles of base per mole of total metal species, respectively.

However, on the basis of potentiometric measurements, Li and co-workers[10] reported that equimolar concentrations of uranyl ion and citric acid react at low

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(2) (a) Abstracted in part from material submitted to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements of the Degree of Doctor of Philosophy. (b) Presented before the Division of Inorganic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.
(3) An appendix giving the experimental data has been deposited as Document No. 8265 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
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