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Bond lengths in bis-salicylaldoximato-nickel.

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A full-matrix least-squares refinement of the crystal structure of bis-salicylaldoximato-nickel has been carried out, using the original three-dimensional Cu $K\alpha$ intensity data of Merritt, Guare & Lessor. The bond lengths in the refined structure are in satisfactory agreement with those found in other substituted salicylaldimine chelates.

One of the first crystal structures to be reported of a metal chelate of a Schiff base was that of bis-salicylaldoximato-nickel (Merritt, Guare & Lessor, 1956). Partial three-dimensional X-ray diffraction intensity data were collected, but the structure was only partially refined. Recently, in comparing the bond distances in a number of salicylaldimine chelates (Lingafelter & Braun, 1966) we have noticed several bond-length discrepancies in bis-salicylaldoximato-nickel, one as large as 0·1 Å, and have therefore completed the refinement, using the Cu $K\alpha$ data of Merritt, Guare & Lessor (1956). Professor Merritt has kindly given us corrected values for the observed structure factors of several reflections. Correct values of F_o are: 113, 20·0; $16,1,\bar{4}$, <0·9; $14,3,\bar{2}$, <0·9; $14,3,\bar{4}$, <0·9; $44\bar{3}$, 19·7; $46\bar{2}$, 7·6. In addition, $56\bar{1}$ and $56\bar{2}$ should be deleted from the list of reflections.

Our refinement has been carried out by full-matrix least squares, using our modification of the program of Busing & Levy (1959). The function minimized was $\Sigma w(F_o - F_c)^2$, with a Hughes (1941) weighting scheme: $\sqrt{w} = 1{\cdot}0$ for $F_o \leq 4{\cdot}0$, $\sqrt{w} = 4{\cdot}0/F_o$ for $F_o > 4{\cdot}0$. The scattering factors used were from Viervoll & Øgrim (1949) for Ni; from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen and carbon; and from McWeeny (1951) for hydrogen.

The hydrogen atoms were placed at the positions of Merritt, Guare & Lessor for all cycles except the final set and for the final set of cycles were placed in recalculated positions, assuming trigonal bonding and a C–H distance of 1·05 Å. The temperature factor for each hydrogen atom was initially assigned equal to that of the atom to which it was attached.

After six cycles of refinement (of the non-hydrogen atoms only) with individual atom isotropic temperature factors, and three with individual anisotropic temperature factors, the value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ (observed reflections only) had decreased from 0·19 to 0·15 and the shifts in parameters in the final cycle were all less than one-half of the estimated standard deviations. Mean values of the standard deviations in positional parameters were: C 0·009 Å; N 0·007 Å; O 0·007 Å.

At this time we received the corrected F_o values from Professor Merritt and carried out a final set of refinement cycles using the revised data. A series of four cycles, refining positions of all atoms, anisotropic temperature factors for the non-hydrogen atoms, and isotropic temperature factors for the hydrogen atoms, reduced R to a final value of 0·14. Although the parameters of the hydrogen atoms were refined, their values are not considered to be significant and are not reported. The final values of the parameters of the non-hydrogen atoms, and their estimated standard deviations, are listed in Table 1. In the final cycle the maximum parameter shifts were 0·9σ in position and 1·0σ in thermal parameters.

Since there are a number of reflections with rather large differences between observed and calculated structure factors, we have carried out an additional series of refinement cycles in which those reflections having $\sqrt{w}\Delta F > 3$ (18 reflections) were omitted. The maximum change in any bond length caused by these omissions was 2σ and the mean was about 1σ.

The bond distances, with their estimated standard deviations, are given in Table 2. Examination of the table shows that the refined bond distances agree more closely with those reported for other substituted salicylaldimine chelates, although the C(9)–N(10) distance still appears to differ considerably. It is doubtful that this difference is significant in view of the fact that the estimated standard deviations are probably underestimated, as is apparent from the magnitudes of the shifts in parameters in the final cycle and in the refinement with 18 reflections omitted.

Although the results of Merritt, Guare & Lessor showed no significant deviation of the molecule from planarity, the present refinement shows a clear deviation from complete planarity. The atoms of the benzene ring and the carbon and oxygen atoms attached to the ring are strictly coplanar (no atom deviates from the least-squares plane by more

Table 1. *Final atomic parameters* (× 10⁴) *and thermal parameters* (× 10²) *with their estimated standard deviations*

The thermal parameters are of the form $\exp [(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*)$

Cell parameters: $a=13{\cdot}83$, $b=4{\cdot}88$, $c=10{\cdot}20$ Å, $\beta=110°26'$
Spacegroup: $P2_1/n$
Number of molecules per cell: 2

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	305 (9)	292 (11)	289 (10)	002 (4)	104 (7)	−003 (4)
O(2)	−0932 (4)	2698 (10)	0002 (5)	308 (19)	264 (21)	231 (19)	006 (16)	076 (15)	−018 (16)
C(3)	−0926 (6)	4386 (16)	1024 (8)	347 (20)	159 (21)	325 (29)	−029 (23)	149 (24)	−059 (25)
C(4)	−1762 (6)	6165 (17)	0815 (8)	276 (26)	330 (34)	323 (30)	−014 (24)	134 (24)	−007 (20)
C(5)	−1785 (7)	7969 (16)	1839 (10)	441 (35)	228 (31)	422 (35)	086 (26)	248 (30)	054 (26)
C(6)	−0980 (6)	8112 (14)	3106 (8)	393 (29)	226 (26)	391 (30)	−035 (20)	241 (26)	−075 (23)
C(7)	−0148 (6)	6394 (17)	3335 (8)	407 (32)	316 (31)	251 (27)	−072 (25)	173 (26)	−071 (26)
C(8)	−0105 (6)	4512 (19)	2332 (11)	259 (26)	330 (28)	419 (37)	−032 (24)	196 (26)	016 (29)
C(9)	0791 (6)	2870 (16)	2615 (7)	332 (28)	293 (31)	267 (26)	044 (23)	115 (22)	−014 (23)
N(10)	0909 (4)	0887 (14)	1770 (5)	240 (20)	288 (25)	204 (19)	−025 (19)	086 (16)	−019 (20)
O(11)	1818 (5)	−0485 (15)	2345 (7)	319 (24)	323 (23)	323 (26)	037 (19)	029 (20)	−076 (20)

Table 2. *Interatomic distances* (Å)

	MGL	LB	SLJ
Ni–O(2)	1·83		1·843 (5)
O(2)–C(3)	1·40	1·313	1·326 (11)
C(3)–C(4)	1·39	1·416	1·401 (11)
C(4)–C(5)	1·41	1·387	1·375 (13)
C(5)–C(6)	1·37	1·382	1·382 (10)
C(6)–C(7)	1·40	1·367	1·376 (11)
C(7)–C(8)	1·42	1·423	1·391 (13)
C(8)–C(3)	1·36	1·415	1·420 (11)
C(8)–C(9)	1·41	1·431	1·418 (11)
C(9)–N(10)	1·40	1·294	1·351 (10)
N(10)–Ni	1·86		1·855 (5)
N(10)–O(11)	1·34		1·363 (9)

MGL	Values of Merritt, Guare & Lessor (1956)
SLJ	Values from present refinement
LB	Mean values from 3-D determinations of salicylaldiminate structures (Lingafelter & Braun, 1966)

than one standard deviation). However, the oxime nitrogen and oxygen atoms lie 0·06 and 0·08 Å, respectively, out of this plane, and the nickel atom is 0·12 Å out of the plane.

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Gitterkonstanten und Raumgruppe einiger Lanthaniden(III)-oxalat-Dekahydrate.

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Unit-cell dimensions, lattice constants and space group $P2_1/c$ have been determined on the basis of Buerger, Weissenberg & Guinier photographs. The complete reduction of the unit cells according to Delaunay leads to a new setting.

Einleitung

In einer Reihe von Untersuchungen seit 1952 wurden die Elementarzellen einer Anzahl von Lanthaniden- und Actiniden(III)-oxalat-Dekahydraten des Typs $M_2(C_2O_4)_3.10H_2O$ bestimmt, [wobei M = La von Gilpin & McCrone (1952) und Jenkins, Moore & Waterman (1965), Nd von Jenkins, Moore & Waterman (1965) und Weigel, Ollendorff, Scherer & Hagenbruch (1966), Sm von Weigel, Ollendorff, Scherer & Hagenbruch (1966), Gd von Jenkins, Moore & Waterman (1965) und Pu von Chackraburtty (1963) und Jenkins, Moore & Waterman (1966) bearbeitet wurde.

Ausgedehntere Untersuchungen an dieser Verbindungsreihe unter Heranziehung von Buerger-, Weissenberg- und Guinieraufnahmen erbrachten, dass die drei Verbindungen $Nd_2(C_2O_4)_3.10H_2O$, $Pm_2(C_2O_4)_3.10H_2O$ und $Sm_2(C_2O_4)_3.10H_2O$ durch zwei verschiedene, aber gleichwertige primitive monokline Elementarzellen beschrieben werden können.

Morphologie

Die Lanthaniden(III)-oxalat-Dekahydrate bilden stäbchenförmige monokline Kristalle nach den Pinakoiden {100}, {010}, abgeschnitten durch das überwiegende Prisma $\{\bar{1}11\}$. Untergeordnet tritt auch noch das Prisma {011} auf. Alle