Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in the Netherlands.

MOLECULAR STRUCTURE DETAILS OF METAL CHELATES

E. C. LINGAFELTER

Department of Chemistry, University of Washington, Seattle, Wash. (USA)

X-ray crystallographic studies make important contributions to our knowledge of the structure of metal complexes and thus to our understanding of their properties. One of the most important and well-known is the determination or proof of coordination configurations. Three examples may be mentioned here: (*a*) the trimeric, octahedral nature of acetylacetonato nickel(II)[1]; (*b*) the distorted tetrahedral coordination of nickel(II) in bis(*N*-isopropylsalicylaldiminato)nickel(II); and (*c*) the pentagonal bipyramidal coordination of uranium(VI) in uranyl acetylacetonate monohydrate[3].

Examination of the details of molecular structures as determined by X-ray crystallography may also be of importance. The purpose of this paper is to present and examine some of the structural details of two sets of metal complexes. These are the chelates formed from acetylacetone and those from substituted salicylaldimines.

At present, structural details of 13 acetylacetone chelates are available[4–16]. A summary of some of these details for those structures which have been published is given in Table I. Except for the Be and Ce compounds, which were studied less accurately by 2-dimensional methods only, the standard deviations in interatomic distances are about .02 Å and the standard deviations in angles are about 1°. The two less accurate structures have been omitted in calculating average values to be

TABLE I

STRUCTURAL DETAILS OF METAL ACETYLACETONATES

Compound	M–O	O–O	O–C	C–C_i	C–C_x	OMO	MOC	OCC_i	CC_iC	OCC_x	δM
$\mathrm{Be(acac)_2}$	1.70	2.68	1.24	1.34	1.55	104°	126°	118°	126°	124°	.12–.52
$\mathrm{Co(acac)_2 \cdot 2H_2O}$	2.06	2.96	1.28	1.42	1.48	92	123	125	128	116	.36
$\mathrm{Ni(acac)_2 \cdot 2H_2O}$	2.02	2.91	1.27	1.41	1.51	92	124	126	127	116	.32
$\mathrm{Zn(acac)_2 \cdot H_2O}$	2.02	2.82	1.29	1.40	1.51	88	127	124	126	117	.25–.40
$\mathrm{Zn(DPM)_2}$	1.96	2.89	1.27	1.41	1.52	95	122	126	127	115	0
$\mathrm{Mn(acac)_3}$	1.87	2.81	1.29	1.38	1.52	97	123	126	125	120	.12–.13
$\mathrm{Cr(acac)_3}$	1.96	2.79	1.26	1.39	1.52	91	127	125	125	115	.11–.19
$\mathrm{VO(acac)_2}$	1.97	2.72	1.28	1.40	1.52	88	129	124	124	116	.30–.38
$\mathrm{Zr(acac)_4}$	2.20	2.67	1.27	1.40	1.52	75	133	124	123	116	.65–.70
$\mathrm{Ce(acac)_4}$	2.40	2.81	1.29	1.40	1.54	72	137	123	127	117	.01–.43

discussed here, but values from the three unpublished structures have been included in the discussion.

A number of general statements may be made concerning the structural details of these molecules.

In all cases, the acetylacetone portion of the chelate ring (*i.e.*, the set of atoms O_1–C_1–C_3–C_2–O_2) is completely planar within the limits of accuracy of the data. However, as shown in the last column of Table I, the metal atom in many cases lies significantly out of this plane. It seems most likely that this effect is due to steric influences and is an indication of considerable flexibility of these molecules. Similarly, the methyl groups are in many cases found to be significantly out of the chelate plane.

The O–C, C–C_i and C–C_x bond distances within the acetylacetonate residues show no significant variations, since for each bond type the difference between maximum and minimum values is four standard deviations or less. The mean values are d(O–C) = 1.28 Å, d(C–C_i) = 1.40 Å, d(C–C_x) = 1.52 Å. However, the distance O–O, the "bite" of the acetylacetonate chelating group, varies significantly, the difference between maximum and minimum being 15 σ.

The variations in the angles within the acetylacetonate residue are slightly greater, the difference between maximum and minimum being 4σ for O–C–C_i, 7σ for C–C_i–C, and 6σ for O–C–C_x. The mean values are (O–C–C_i) = 125.3°, (C–C_i–C) = 124.5°, (O–C–C_x) = 115.7°. The slight variations in O–C–C_i are not significant. Comparison of values in Table I show that the variations in C–C_i–C are directly correlated with the variations in O–O. The variations in O–C–C_x are probably due to steric effects. It thus appears that the only effect of varying the metal ion is a variation in the O–O "bite" distance, which is accomplished primarily by changes in the C–C_i–C angle. This variation in the O–O distance is clearly not due to differences in metal radii, since, for example, the two largest values of O–O are found for Co and Ni, which have intermediate radii. However, it would appear that the O–O distance is shortened by increased oxidation state of the metal, as shown in Table II.

Structural details of 13 substituted salicylaldimine chelates with the three metal ions Ni^{2+}, Cu^{2+} and Pd^{2+} are available[17–29]. A summary of some of these

TABLE II

O–O DISTANCE IN ACETYLACETONATE CHELATES

M	*O–O, Å*
Co(II)	2.96
Ni(II)	2.91
Zn(II)	2.89, 2.82
Cr(III)	2.79
Mn(III)	2.81
V(IV)	2.72
Zr(IV)	2.67

details is given in Table III. The Ni–N–iso-C_3H_7–chelate and all of the Cu chelates have been studied with 3-dimensional data and have standard deviations of about .02 Å in interatomic distances and about 1° in angles. The others are less accurate.

TABLE III

STRUCTURAL DETAILS OF METAL CHELATES OF SUBSTITUTED SALICYLALDIMINES

M	Subst.	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_6	C_6–C_1	C_1–C_7	C_2–C	C_7–N	δM
Ni	none	1.41	1.41	1.37	1.40	1.38	1.41	1.44	1.32	1.29	0.4
Ni	N–CH_3	1.36	1.41	1.42	1.38	1.40	1.40	1.46	1.28	1.30	.37
Ni	N-iso-C_3H_7	1.44	1.43	1.41	1.40	1.38	1.44	1.45	1.30	1.30	.16
Ni	N–OH	1.36	1.39	1.41	1.37	1.40	1.41	1.42	1.40	1.40	.02
Ni	5–Cl, N–OH	1.41	1.39	1.39	1.41	1.42	1.40	1.43	1.30	1.28	*
Cu	N–CH_3	1.42	1.40	1.39	1.40	1.37	1.39	1.44	1.32	1.31	0
Cu	N–C_6H_5	1.40	1.42	1.40	1.37	1.37	1.42	1.44	1.31	1.30	.42
Cu	N–OH	1.40	1.39	1.38	1.36	1.36	1.44	1.45	1.36	1.25	.05
Cu	5–Cl, N–OH	1.44	1.40	1.38	1.40	1.36	1.40	1.44	1.33	1.26	.04
Pd	N–C_2H_5	1.40	1.40	1.40	1.42	1.42	1.39	1.49	1.32	1.31	.30
Pd	N–n–C_4H_9	1.39	1.39	1.38	1.38	1.39	1.38	1.40	1.58	1.42	.20
Pd	N–OH	1.39	1.40	1.41	1.40	1.40	1.41	1.41	1.32	1.28	*
Pd	5–Cl, N–OH	1.41	1.40	1.40	1.40	1.41	1.40	1.45	1.31	1.30	*

* not available.

In all of the 3-dimensional determinations the entire salicylaldimine residue appears to be planar, while two of the 2-dimensional determinations show considerable deviations from planarity. As with the acetylacetonates, the metal atom in many cases lies significantly out of this plane, again showing flexibility at the metal.

In the entire group of 13 structures, the range from maximum to minimum values of the aromatic C–C bonds is 1.36 to 1.46 Å (*i.e.*, $\sim 5\sigma$) and the mean value is 1.40 Å. This same range and mean value is found for the 3-dimensional sub-group. Closer examination of the values for individual bonds shows a consistent tendency for the three bonds closest to the chelate ring to be slightly longer than the other three. Thus the mean values for the 3-dimensional sub-group are C_6–C_1, 1.42; C_1–C_2, 1.42; C_2–C_3, 1.41; C_3–C_4, 1.39; C_4–C_5, 1.39; C_5–C_6, 1.37 Å and for the entire group are C_6–C_1, 1.41; C_1–C_2, 1.40; C_2–C_3, 1.40; C_3–C_4, 1.40; C_4–C_5, 1.39; C_5–C_6, 1.39 Å. It is not certain whether this is a real structural difference or an indication of some unidentified systematic error in the determinations.

The C_1–C_7 bond shows no significant variation. The 3-dimensional subgroup gives a range of 3σ and a mean value 1.45 Å, the entire group gives a range of .10 Å and a mean value of 1.44 Å. It thus appears that this bond is significantly longer than the C_1–C_2 bond and the C–C_i bond in the acetylacetonate chelates.

The C_2–O bond shows no significant variation among the 3-dimensional determinations, with a range of 3.5 σ and a mean value of 1.32 Å. This length is significantly longer than the 1.28 value found in the acetylacetonates. Two of the less accurate determinations give lengths (1.40 and 1.58 Å) which are considerably greater. It is suggested that these are probably in error. Although in the case of the Pd(*N*-*n*-Bu-sim)$_2$ the difference is about six times the estimated standard deviation of the 2-dimensional determination.

The C_7–N bond results show the same pattern of variation as the C_2–O bond, with the same two compounds giving large values. For the 3-dimensional determinations, the range is 2.5 σ and the mean value is 1.29 Å.

Consideration of all of the bond lengths in the chelate ring shows that, as might be expected from the relative electronegativities of oxygen and nitrogen, the form $^-\mathrm{O{-}C_2{=}C_1{-}C_7{=}N}$ is more important than the form $\mathrm{O{=}C_2{-}C_1{=}C_7{-}N^-}$. This follows from two observations. First, C_7–N is found to be shorter than C_2–O, although for bonds of the same order, C–N is longer than C–O. Thus C_7–N has more double-bond character than C_2–O. Second, C_1–C_7 is found to be slightly longer than C_1–C_2, indicating less double-bond character.

In summary, the following generalizations have been suggested:

(1) both the acetylacetonate and salicylaldiminate chelating agents remain quite closely planar;

(2) the metal atom may deviate from the plane of the chelate ring by as much as 0.7 Å, giving the molecules considerable flexibility at the metal;

(3) bond distances appear to be constant within the chelating agent, independent of the nature of the metal;

(4) the O–O distance, the "bite" of the acetylacetonate chelating agent shows considerable variation, apparently decreasing with increasing oxidation state of the metal;

(5) determinations of structures from 2-dimensional data may give some bond lengths which are in error by many times the estimated standard deviations.

The author wishes to acknowledge the assistance of Dr. H. Montgomery, Dr. B. Morosin and Mrs. Fay Pullen in the preparation of material for this paper and the financial support of the U.S. Public Health Service and the U.S. National Science Foundation.

REFERENCES

1 G. J. Bullen, R. Mason and P. Pauling, *Nature*, 189 (1961) 291.
2 M. R. Fox, P. L. Orioli, E. C. Lingafelter and L. Sacconi, *Nature*, 197 (1963) 1104.
3 E. Frasson, G. Bombieri and C. Panattoni, *This Volume*, p. 145.
4 V. Amirthalingam, V. M. Padmanabhan and J. Shankar, *Acta Cryst.*, 13 (1960) 201, Be(AcAc)$_2$.
5 G. J. Bullen, *Acta Cryst.*, 12 (1959) 703, Co(AcAc)$_2$ · 2H$_2$O.
6 H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, 17 (1964) 1481, Ni(AcAc)$_2$ · 2H$_2$O.
7 L. F. Dahl, unpublished results Cu(AcAc)$_2$.
8 M. R. Truter and I. Robertson, unpublished results Cu(3–CH$_3$–AcAc)$_2$.
9 H. Montgomery and E. C. Lingafelter, *Acta Cryst*, 16 (1963) 748, Zn(AcAc)$_2$ · H$_2$O.
10 F. A. Cotton and J. S. Wood, *Inorg. Chem.*, 3 (1964) 245, Zn (dipivaloylmethane)$_2$.
11 B. Morosin and J. R. Brathovde, *Acta Cryst.*, 17 (1964) 705, Mn(AcAc)$_3$.

12 B. MOROSIN, unpublished results Cr(AcAc)$_3$.
13 J. IBALL, unpublished results Fe(AcAc)$_3$.
14 R. P. DODGE, D. H. TEMPLETON AND A. ZALKIN, *J. Chem. Phys.*, 35 (1961) 55, VO(AcAc)$_2$.
15 J. V. SILVERTON AND J. L. HOARD, *Inorg. Chem.*, 2 (1963) 243, Zr(AcAc)$_4$.
16 B. MATKOVIĆ AND D. GRDENIĆ, *Acta Cryst.*, 16 (1963) 456, Ce(AcAc)$_4$.
17 J. M. STEWART AND E. C. LINGAFELTER, *Acta Cryst.*, 12 (1959) 842, Ni(sim)$_2$.
18 E. FRASSON, C. PANATTONI AND L. SACCONI, *J. Phys. Chem.*, 63 (1959) 1908, Ni(*N*–CH$_3$–sim)$_2$.
19 L. L. MERRITT, JR., C. GUARE AND A. E. LESSOR, JR., *Acta Cryst.*, 9 (1956) 253, Ni(*N*–OH–sim)$_2$.
20 M. R. FOX, P. L. ORIOLI, E. C. LINGAFELTER AND L. SACCONI, *Acta Cryst.*, 17 (1964) 1159, Ni(*N*–iso–C$_3$H$_7$–sim)$_2$.
21 S. H. SIMONSEN, unpublished results Ni(*N*–OH–5–Cl–sim)$_2$.
22 E. C. LINGAFELTER, G. L. SIMMONS, B. MOROSIN, C. SCHERINGER AND C. FREIBURG, *Acta Cryst.*, 14 (1961) 1222, Cu(*N*–CH$_3$–sim)$_2$.
23 L. WEI, R. M. STOGSDILL AND E. C. LINGAFELTER, *Acta Cryst.*, 17 (1964) 1058, Cu(*N*–C$_6$H$_5$–sim)$_2$.
24 M. A. JARSKI AND E. C. LINGAFELTER, *Acta Cryst.*, 17 (1964) 1109, Cu(*N*–OH–sim)$_2$.
25 P. L. ORIOLI, E. C. LINGAFELTER AND B. W. BROWN, *Acta Cryst.*, 17 (1964) 1113, Cu(*N*–OH–5–Cl–sim)$_2$.
26 E. FRASSON, C. PANATTONI AND L. SACCONI, *Acta Cryst.*, 17 (1964) 85, Pd(*N*–C$_2$H –sim)$_2$.
27 E. FRASSON, C. PANATTONI AND L. SACCONI, *Acta Cryst.*, 17 (1964) 477, Pd(*N*–*n*–C$_4$H$_9$–sim)$_2$.
28 S. H. SIMONSEN, unpublished results Pd(*N*–OH–sim)$_2$.
29 S. H. SIMONSEN, unpublished results Pd(*N*–OH–5–Cl–sim)$_2$.