Interatomic Distances and Angles in Metal Chelates of Acetylacetone and Salicylaldimine

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Abstract: Interatomic distances and angles in published (and some unpublished) structures of acetylacetone and salicylaldimine chelates have been compared and a number of general relations noted. Bond distances in both chelating agents are found to agree very closely with distances calculated from simple Hückel π-electron molecular orbital bond orders. Metal–oxygen distances for most transition metal ions are shorter than the ionic radii sums, but not for Be(II), Al(III), Zr(IV), or Ce(IV). The "bite" of the chelating agents is significantly variable and correlates best with the ratio of ionic radius to oxidation number of the metal.

In view of the considerable number of X-ray diffraction structural determinations of metal chelates of acetylacetone (acac) and salicylaldimine (sim) which have been recently completed, it seems appropriate to summarize the structural information which has been obtained and to point out some regularities which appear in the structures. Table I lists the complexes which have been included in this survey.[1-29] The acac survey (part I, below) is concerned mainly with the structural similarities or differences in relation to a change of the metal ion, keeping the ligand unmodified for the most part. The sim survey (part II), on the other hand, is more concerned with structural similarities or differences in relation to substituents on the ring or on the aldimine nitrogen, since accurate three-dimensional determinations have been carried out only on complexes containing Ni and Cu.

Table I. Complexes Included in Survey

Acetylacetone (3-D)[a]	Ref	Salicylaldimine (3-D)[a]	Ref
$Mn(acac)_3$	1	α-Ni(N-methylsim)$_2$	16
$Zn(acac)_2 \cdot H_2O$	2	Ni(N-isopropylsim)$_2$	17
Cu(3-methylacac)$_2$	3	Ni(N-isopropyl-3-methylsim)$_2$	18
$Ni(acac)_2 \cdot 2H_2O$	4	Cu(N-phenylsim)$_2$	19
$Cr(acac)_3$	5	α-Cu(N-methylsim)$_2$	20
$Al(acac)_3$	6a	Cu(N-hydroxysim)$_2$	21
$Co(acac)_3$	6b	Cu(N-hydroxy-5-chlorosim)$_2$	22
μ-[CrPh$_2$PO$_2$(acac)$_2$]$_2$	7	Ni(N-hydroxysim)$_2$	23
$VO(acac)_2$	8		
$Zr(acac)_4$	9	Salicylaldimine (2-D)[b]	
$Fe(acac)_3$	10		
$Cu(acac)_2$	11		
Zn(dipivaloylmethanido)$_2$	12	Ni(sim)$_2$	24
		β-Ni(N-methylsim)$_2$	25
Acetylacetone (2-D)[b]		Ni(N-hydroxysim)$_2$	26
		Ni(N-hydroxy-5-chlorosim)$_2$	27a
		Pd(N-ethylsim)$_2$	28
$Co(acac)_2 \cdot 2H_2O$	13	Pd(N-butylsim)$_2$	29
$Be(acac)_2$	14	Pd(N-hydroxysim)$_2$	27b
$Ce(acac)_4$	15	Pd(N-hydroxy-5-chlorosim)$_2$	27c

[a] Three-dimensional determinations. [b] Two-dimensional determinations.

Part I. Interatomic Distances and Angles in Acetylacetone Complexes

In order to assess the constancy or variability of the several measured distances and angles in the acac complexes and to determine the correlations between various distances and angles, compilations of one value for each "chemically unique" distance or angle for each acac ring were made for the three-dimensional and two-dimensional structure determinations. These compilations are shown in Tables II and III, the labeling of atoms is shown in Figure 1, and the identification of the numbered complexes is shown in Table I. In calculating the averages, it would have been best to weight each measurement according to its experimental standard deviation; however, this was precluded by a lack of consistent reporting of standard deviations. Reported standard deviations were generally 0.01 to 0.02 A for the distances and 0.5 to 1.5° for angles.

From Table II it is seen that the ranges for the distances O–C, C–C$_i$, and C–C$_x$ are 0.062, 0.054, and 0.073 A, respectively. These ranges are three to four

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Table II. Acetylacetonate Three-Dimensional Determinations

		Interatomic distances, A					Interatomic angles, deg				
Complex	Ring	M–O	O–O	O–C	C–C$_i$	C–C$_x$	OMO	MOC	OCC$_i$	CC$_i$C	OCC$_x$
1	1	1.861	2.802	1.277	1.395	1.530	97.75	123.05	125.61	122.74	113.51
	2	1.878	2.805	1.307	1.358	1.497	96.72	123.20	124.37	127.52	113.52
	3	1.881	2.809	1.281	1.382	1.525	96.65	123.23	125.96	124.37	114.10
2	1	2.032	2.836	1.297	1.389	1.488	88.50	126.90	124.40	126.80	116.20
	2	2.008	2.790	1.286	1.402	1.532	88.00	127.30	124.10	125.10	117.00
3	1	1.908	2.759	1.285	1.410	1.497	92.60	127.14	125.45	122.12	113.75
4	1	2.018	2.913	1.272	1.412	1.510	92.40	123.60	125.50	126.60	115.90
5	1	1.943	2.786	1.250	1.394	1.535	91.66	126.63	125.28	124.06	114.24
	2	1.957	2.791	1.276	1.387	1.504	90.95	127.00	124.67	125.60	114.87
	3	1.955	2.781	1.262	1.382	1.513	90.67	127.13	124.25	125.61	116.14
6a	1	1.891	2.722	1.294	1.402	1.545	91.98	127.72	125.30	121.54	113.86
	2	1.898	2.735	1.277	1.373	1.553	91.87	126.27	126.77	121.15	114.44
	3	1.886	2.721	1.279	1.365	1.544	91.68	127.53	123.89	125.02	114.75
6b	1	1.886	2.837	1.272	1.385	1.561	97.54	121.81	127.96	122.24	112.60
	2	1.905	2.862	1.273	1.384	1.544	97.37	121.52	127.71	123.73	112.95
	3	1.902	2.851	1.261	1.378	1.527	97.05	121.99	126.89	124.87	113.22
7	1	1.956	2.805	1.260	1.405	1.535	91.60	127.00	124.50	123.90	116.10
	2	1.947	2.761	1.258	1.381	1.536	90.30	126.30	128.00	121.00	113.90
	3	1.960	2.774	1.284	1.409	1.495	90.10	129.00	123.90	124.30	117.30
	4	1.951	2.790	1.272	1.385	1.511	91.30	126.10	126.30	123.70	114.20
8	1	1.965	2.710	1.285	1.395	1.520	87.20	129.00	123.90	123.30	116.10
	2	1.970	2.734	1.285	1.400	1.515	87.90	129.10	123.60	124.40	115.70
9	1	2.206	2.683	1.264	1.395	1.531	74.93	132.39	123.83	122.79	115.30
	2	2.190	2.665	1.276	1.404	1.502	74.97	133.77	123.43	122.12	116.93
10	1	1.992	2.734	1.272	1.376	1.524	86.71	129.68	125.06	123.76	113.89
	2	1.989	2.746	1.259	1.374	1.519	87.33	129.19	124.27	125.29	116.11
	3	1.995	2.751	1.245	1.381	1.546	87.15	128.84	124.19	125.19	114.64
11	1	1.921	2.801	1.260	1.404	1.545	93.60	124.50	127.80	120.80	114.80
12	1	1.962	2.886	1.274	1.405	1.517	94.70	121.80	125.80	127.00	114.70
Average		1.959	2.781	1.274	1.390	1.524	90.73	126.51	125.30	124.02	114.85
Std dev for an individual measurement											
		0.079	0.057	0.014	0.014	0.019	5.44	3.05	1.40	1.81	1.26
Std dev for the average											
		0.015	0.011	0.003	0.003	0.003	1.01	0.57	0.26	0.34	0.23
Range		0.345	0.248	0.062	0.054	0.073	22.82	12.25	4.57	6.72	4.70

Table III. Acetylacetonate Two-Dimensional Determinations

		Interatomic distances, A					Interatomic angles, deg				
Complex	Ring	M–O	O–O	O–C	C–C$_i$	C–C$_x$	OMO	MOC	OCC$_i$	CC$_i$C	OCC$_x$
13	1	2.055	2.956	1.275	1.420	1.480	92.0	123.4	124.7	127.9	116.0
14	1	1.680	2.683	1.215	1.315	1.550	106.0	126.0	121.0	126.0	123.5
	2	1.725	2.719	1.265	1.365	1.540	104.0	128.5	117.0	128.0	126.5
	3	1.715	2.703	1.230	1.335	1.525	104.0	122.5	113.5	128.0	124.5
	4	1.690	2.627	1.250	1.350	1.565	102.0	126.0	120.0	121.0	123.0
15	1	2.395	2.870	1.310	1.410	1.550	73.0	134.5	122.5	128.0	118.5
	2	2.365	2.800	1.290	1.385	1.530	73.0	137.0	122.0	129.0	117.0
	3	2.390	2.770	1.285	1.410	1.550	71.0	138.5	123.0	126.0	115.5
	4	2.430	2.800	1.275	1.410	1.520	71.0	137.0	122.5	126.0	115.0
Average		2.049	2.770	1.266	1.378	1.534	88.4	130.4	120.7	126.7	119.9
Std dev for an individual measurement											
		0.327	0.095	0.028	0.036	0.024	15.2	6.0	3.3	2.3	4.2
Std dev for the average											
		0.109	0.032	0.009	0.012	0.008	5.1	2.0	1.1	0.8	1.4
Range		0.750	0.329	0.095	0.105	0.085	35.0	16.0	11.2	8.0	11.5

times the estimated standard deviations of the distances. Similarly the ranges of 4.57, 6.72, and 4.70° for the angles OCC$_i$, CC$_i$C, and OCC$_x$ are three to four times the estimated standard deviations of the angles. It can therefore be concluded that within experimental error O–C, C–C$_i$, C–C$_x$, OCC$_i$, CC$_i$C, and OCC$_x$ are essentially invariant among the 13 three-dimensionally determined acac complexes. Conversely, the large ranges for M–O (0.345 A), O–O (0.248 A), OMO (22.82°), and MOC (12.25°), which are from 8 to 20 times the estimated standard deviations, illustrate their variability among these acac complexes. In order to assess the interdependence of these four variable interatomic distances and angles, the correlation coefficient for each pair was calculated. Five of the six correlation coefficients are substantial: −0.92 (OMO and MOC), −0.92 (OMO and M–O), −0.85 (MOC and O–O), 0.71 (MOC and M–O), and 0.71 (OMO and O–O). The correlation coefficient is only 0.17 for M–O and O–O.

The variable distances, M–O and O–O, were examined in relationship to various properties of the coordi-

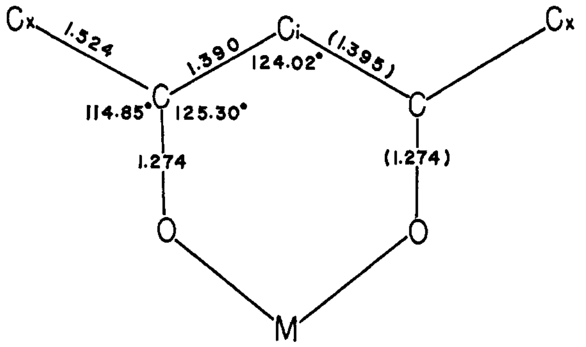

Figure 1. Acetylacetone complex showing average measured nonvariable interatomic distances and angles (calculated interatomic distances in parentheses).

nated metal ions. The average values of these distances for two and three dimensionally determined acac chelates are tabulated in Table IV along with the oxidation state of the metal ion (Q), the Pauling crystal radius[30] of the metal ion (r), and r/Q. Since no value of the Cu(II) radius is available in Pauling's crystal radii, the value of 0.55 A was taken as a reasonable estimate.[31]

Table IV. Acetylacetonate Two- and Three-Dimensional Determinations

Compound	Metal	Oxidn state, Q	Crystal radius, r, A	r/Q	Distance, A O–O	M–O
1	Mn	3	0.66	0.22	2.805	1.872
2	Zn	2	0.74	0.37	2.813	2.020
3	Cu	2	0.55	0.275	2.759	1.908
4	Ni	2	0.72	0.36	2.913	2.018
5	Cr	3	0.69	0.23	2.786	1.951
6a	Al	3	0.50	0.17	2.726	1.892
6b	Co	3	0.63	0.21	2.850	1.898
7	Cr	3	0.69	0.23	2.783	1.954
8	V	4	0.60	0.15	2.722	1.968
9	Zr	4	0.80	0.20	2.674	2.198
10	Fe	3	0.64	0.21	2.744	1.992
11	Cu	2	0.55	0.275	2.801	1.921
12	Zn	2	0.74	0.37	2.886	1.962
13	Co	2	0.74	0.37	2.956	2.055
14	Be	2	0.31	0.16	2.683	1.703
15	Ce	4	1.01	0.25	2.810	2.400

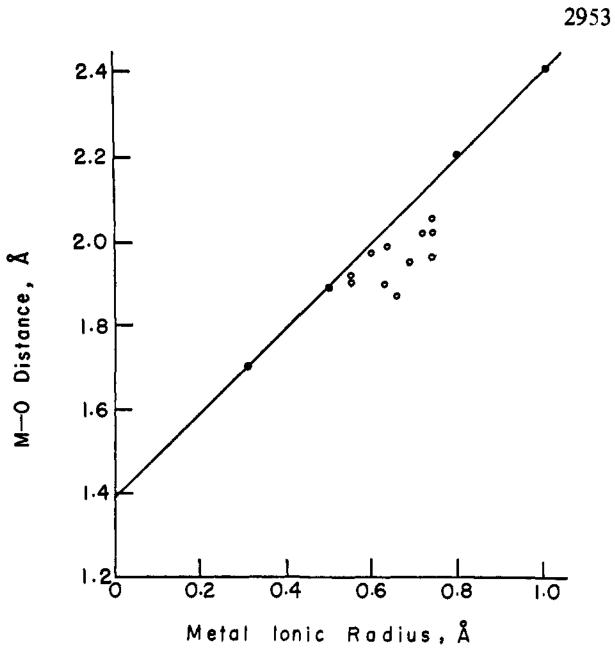

Figure 2. Acetylacetone M–O distances: ●, metal ions having inert gas configurations; ○, transition metal ions (see Table IV for identification of points).

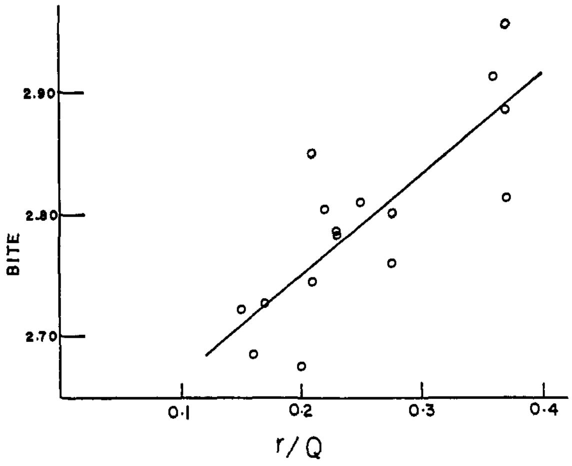

Figure 3. Acetylacetone "bite" distance, *i.e.*, O–O, in angstrom units (see Table IV for identification of points).

Figure 2 illustrates the relationship between the M–O distance and crystal radius. The four darkened circles correspond to metal ions which have an inert gas configuration: Be(II), Al(III), Zr(IV), and Ce(IV). These four ions very closely follow the least-squares line (M–O) = 1.394 + 0.999r, with a standard deviation of 0.004 A for M–O and a correlation coefficient of 1.000 between M–O and r. Thus, for the metal ions having inert gas configurations, the metal–oxygen distance in acetylacetonates is, within the accuracy of the measurements, given by the sum of the Pauling crystal radii. This should not, of course, be interpreted as indicating that the metal–oxygen interaction is purely ionic. For all of the other metal ions studied, ranging from V(IV) with one d electron, to Zn(II) with ten d electrons, the metal–oxygen distance in the acetylacetonate is less than the sum of the Pauling crystal radii. This probably indicates an increased covalency in the acetylacetonates compared with the crystals used in the establishment of Pauling's radii.

The O–O distance, which may be called the "bite" of the chelating agent acac, was examined in its relationship to the oxidation state, the crystal radius and the (Q − 1)th ionization potential of the metal ion and to the measured M–O distance and O–M–O angle. Calculation of correlation coefficients between the bite and these five properties or various combinations of these five properties indicated that the bite can best be correlated (although the correlation is not very good) with the ratio of the crystal radius of the metal ion to its oxidation state. As shown in Figure 3, the bite follows the least-squares line: bite = 2.584 + 0.832(r/Q), with a standard deviation of 0.046 A for the bite and a correlation coefficient of 0.81 between the bite and r/Q. This relationship appears to be a simple way of estimating the general trend of bite with change in

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Table V. Salicylaldiminate Three-Dimensional Determinations[a]

Complex	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_7–N	C_2–O	M–N	M–O	O–N
16 d	1.413	1.375	1.394	1.322	1.375	1.447	1.428	1.307	1.341	1.922	1.851	2.747
σ	0.020	0.022	0.022	0.022	0.022	0.020	0.022	0.018	0.016	0.012	0.012	
17 d	1.456	1.406	1.398	1.388	1.379	1.425	1.422	1.298	1.300	1.990	1.894	2.841
σ	0.008	0.010	0.011	0.010	0.010	0.010	0.009	0.009	0.009	0.005	0.005	
17 d	1.421	1.448	1.407	1.396	1.379	1.452	1.481	1.303	1.294	1.950	1.898	2.830
σ	0.016	0.010	0.013	0.019	0.011	0.012	0.010	0.010	0.011	0.009	0.004	
18 d	1.412	1.413	1.380	1.388	1.358	1.424	1.419	1.287	1.310	1.920	1.837	2.707
σ	0.004	0.004	0.005	0.005	0.005	0.004	0.004	0.004	0.003	0.002	0.002	
19 d	1.399	1.422	1.396	1.373	1.371	1.421	1.436	1.302	1.313	1.993	1.878	2.772
σ	0.006	0.006	0.006	0.008	0.007	0.005	0.006	0.005	0.004	0.004	0.003	
20 d	1.416	1.403	1.388	1.404	1.373	1.393	1.440	1.305	1.320	1.989	1.901	2.778
σ	0.017	0.017	0.017	0.017	0.017	0.017	0.017	0.015	0.015	0.012	0.012	
21 d	1.40	1.39	1.38	1.36	1.36	1.44	1.45	1.25	1.36	1.94	1.92	2.763
σ	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	
22 d	1.438	1.397	1.376	1.395	1.360	1.402	1.441	1.256	1.326	1.957	1.908	2.776
σ	0.017	0.018	0.017	0.019	0.018	0.015	0.017	0.014	0.013	0.009	0.009	
23 d	1.414	1.400	1.374	1.385	1.378	1.400	1.433	1.336	1.337	1.851	1.841	2.697
σ	0.011	0.013	0.014	0.011	0.013	0.015	0.013	0.012	0.011	0.006	0.006	
Weighted av	1.415	1.415	1.388	1.384	1.367	1.423	1.430	1.295	1.312	1.936	1.862	2.768
σ_I	0.018	0.015	0.009	0.015	0.009	0.012	0.018	0.015	0.009	0.039	0.030	0.048
σ_A	0.006	0.005	0.003	0.005	0.003	0.004	0.006	0.005	0.003	0.013	0.010	0.016
Range	0.056	0.073	0.033	0.082	0.021	0.059	0.059	0.086	0.066	0.142	0.08	0.143

[a] Interatomic distances and their standard deviations in angstrom units.

the coordinated metal ion, although the bite of a chelate is certainly determined by a more complex relationship. For example, as shown below in comparing the bite of acac with that of sim, the bite for a given metal ion may depend upon coordination number and configuration. In Figure 3, coordination numbers of 4, 5, 6, and 8 have been included. A corresponding calculation, using only the eight chelates having a coordination number of 6, gives a correlation coefficient of 0.91 between the bite and r/Q and a standard deviation of 0.034 A for the bite.

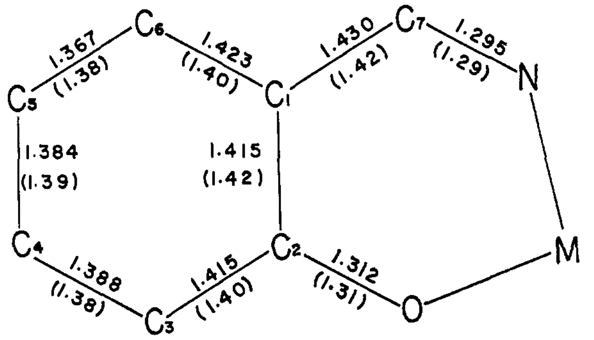

Figure 4. Salicylaldimine complex showing average measured nonvariable interatomic distances (calculated interatomic distances in parentheses).

Returning to the invariable interatomic distances of the acac chelates, it is noted that the average ring C–C_i distance of 1.390 A is approximately equal to the C–C distance in benzene and that the average C–O distance of 1.274 A is intermediate between single and double bond lengths. This is consistent with a π-electron system including the carbon and oxygen atoms of the chelate ring.

Although a number of Hückel molecular orbital calculations on the acetylacetonate ion and on acetylacetone chelates have been reported,[32-35] in no case have the bond orders been reported. We have therefore carried out the bond-order calculation, using the simple Hückel molecular orbital treatment of the π-electron system of the acetylacetonate ion, five atoms and six π electrons. This treatment (completely ignoring the metal ion) is considered to be warranted by the empirical observation that these bond lengths are independent of the metal ion, by the conclusions of Maki and McGarvey[36] from the paramagnetic resonance spectrum of copper(II) acetylacetonate, and by the conclusions of Fackler, Cotton, and Barnum.[34]

To give consistency with the calculated charge distribution, a "resonance integral" of 1.4β for the O–C bond and a Coulomb integral of $\alpha + 1.2\beta$ for the oxygen atom were used. The calculated bond orders were converted to bond lengths by the equations of Bernstein.[37] The calculated bond lengths of 1.274 A for O–C and 1.395 A for C–C_i are in excellent agreement with the average measured values of 1.274 and 1.390 A, despite the usual marginal accuracy of the Hückel molecular orbital method.

Part II. Interatomic Distances in Salicylaldimine Complexes

Interatomic distances are compiled in Table V and VI for the three- and two-dimensional structure determinations of sim chelates, and the labeling of the atoms is shown in Figure 4. For the three-dimensional structure determinations, the average was calculated by weighting each measurement by $1/\sigma^2$. In addition to the average bond length, these tables show the standard deviation for an individual measurement (σ_I), the standard deviation for the average (σ_A), and the range.

For the bonds of the salicylaldimine residue, it is seen from Table V that the empirical σ_I values are from 0.009

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Table VI. Salicylaldiminate Two-Dimensional Determinations[a]

Complex	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_7–N	C_2–O	M–N	M–O	O–N
24	1.407	1.409	1.374	1.403	1.384	1.414	1.438	1.291	1.316	1.840	1.840	2.687
25	1.36	1.41	1.42	1.38	1.40	1.40	1.46	1.30	1.28	1.90	1.80	2.750
26	1.36	1.39	1.41	1.37	1.40	1.41	1.42	1.40	1.40	1.86	1.83	2.742
27a	1.41	1.39	1.39	1.40	1.42	1.40	1.43	1.28	1.30	1.86	1.84	2.706
28	1.40	1.40	1.40	1.42	1.42	1.39	1.49	1.31	1.32	1.86	1.94	2.711
29	1.39	1.39	1.38	1.38	1.39	1.38	1.40	1.42	1.58	2.01	2.00	3.160
27b	1.41	1.40	1.40	1.41	1.40	1.39	1.41	1.28	1.32	1.94	1.99	2.851
27c	1.41	1.40	1.40	1.40	1.41	1.40	1.45	1.30	1.31	1.99	2.02	2.933
Average	1.393	1.399	1.397	1.395	1.403	1.398	1.437	1.323	1.353	1.907	1.907	2.817
σ_I	0.023	0.008	0.014	0.017	0.014	0.011	0.028	0.054	0.099	0.065	0.091	0.161
σ_A	0.008	0.003	0.005	0.006	0.005	0.004	0.010	0.019	0.035	0.023	0.032	0.057
Range	0.05	0.02	0.046	0.05	0.036	0.034	0.09	0.14	0.30	0.17	0.22	0.473

[a] Interatomic distances in angstrom units.

to 0.018 A. This indicates that within experimental error these bond lengths are constant for the eight three-dimensional salicylaldiminates (nine individually measured rings), despite the various substituents on the ring and on the nitrogen. Conversely, the σ_I values for M–N, M–O, and O–N are 0.039, 0.030, and 0.048 A, respectively, indicating significant variations due to differences in the coordinated metal ion and differences in the coordination configuration. The O–N distance, which may be called the bite of this chelating agent, is further discussed below.

Between the three- and two-dimensional average bond lengths of the salicylaldimine residue there are differences of up to 12 times the standard deviation of the average three-dimensional bond. This is presumably indicative of substantial error in the two-dimensional structures. This conclusion has also been reached by Srivastava and Lingafelter[23] in comparing their three-dimensional refinement of bis(salicylaldoximato)nickel with the original two-dimensional refinement of the same data which was carried out by Merritt, Guare, and Lessor.[26]

An interesting feature of the three-dimensional sim bond lengths is that the three C–C bonds which are most distant from the metal (C_3–C_4, C_4–C_5, and C_5–C_6) all have an average length less than 1.39 A, while the four C–C bonds which are nearest the metal (C_6–C_1, C_1–C_2, C_2–C_3, and C_1–C_7) all have an average length greater than 1.41 A. This phenomenon was at first suspected to be due to systematic errors in the crystal structure determinations. However, a quantum mechanical calculation of the sim bond lengths has illustrated a more probable explanation of this phenomenon. The simple Hückel molecular orbital method was applied to the π-electron system of the salicylaldiminate ion, nine atoms and ten π electrons. To give consistency with the calculated charge distribution, Coulomb integrals of $\alpha + 1.4\beta$ for the oxygen atom and $\alpha + 0.4\beta$ for the nitrogen atom and resonance integrals of 1.4β for the C_2–O bond and β for the C_7–N bond were used. For comparison with the average measured bond distances, the calculated bond orders were converted to bond distances by the equations of Bernstein.[37] The excellent agreement between the measured and calculated bond distances is shown in Figure 4. It is thus apparent that there is a very real difference in C–C bond lengths between the "near" and "far" sides of the benzene ring. A similar calculation for the salicylaldehyde chelating agent resulted in C–C bond lengths which were within 0.002 A of the bond lengths calculated for salicylaldimine.

Two observations indicate that the difference in C–C bond lengths between the near and far sides of the benzene ring is unrelated to the chelation to a heavy metal ion. First, the above MO calculation was made without consideration of the presence of any metal ion. Secondly, a similar difference in C–C bond lengths, although not as pronounced as that mentioned above, is shown in the free chelating agents salicylic acid,[38] N-5-chlorosalicylidineaniline,[39] and 2-chloro-N-salicylideneaniline.[40] The latter molecule, for example, has all C–C bonds greater than 1.391 A for the near side and less than 1.388 A for the far side.

Having examined the structural details of the two complexing agents acac and sim, some final comparisons can be made. The C_2–O length in sim (1.31 A, calculated and measured) is found to be significantly longer than the C–O length in acac (1.27 A, calculated and measured). It is interesting to note that in bis(salicylaldehydato)copper,[41] which is the only three-dimensional salicylaldehyde structure available for comparison, the C_2–O length of 1.31 A (1.30 A, calculated) is equal to the C_2–O length of sim, while the C_7–O length of 1.28 A (1.26 A, calculated) is nearly equal to the C–O length of acac. Analogous to this difference in bond order between the C_2–O and C_7–O bonds of the salicylaldehyde complex, there is a marked difference in bond order between the C_2–O and C_7–N bonds of the average salicylaldimine complex. The C_2–O bond order is 0.52 and the C_7–N bond order is 0.84, calculated from the average measured interatomic distances of 1.312 and 1.295 A by Bernstein's equations.

It is also of interest to compare the bite distances for acac and sim. For a given metal, these chelates appear to have the same bite in complexes having the same coordination configuration. For example, for planar-coordinated Cu(II) the bite is 2.78, 2.77, and 2.75 A in acac, sim, and salicylaldehyde, respectively. However, for a given metal, a change in the coordination configuration changes the bite considerably. For example, for planar-coordinated Ni(II) the average bite is 2.72 A [α-Ni(N-methylsim)$_2$,[16] Ni(N-hydroxy-

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sim)$_2$,[23] and Ni(N-isopropyl-3-methylsim)$_2$];[18] for tetrahedrally coordinated Ni(II) the bite is 2.84 A [Ni(N-isopropylsim)$_2$];[17] and for octahedrally coordinated Ni(II) the bite is 2.91 [Ni(sal)$_2$·2H$_2$O],[42] 2.91 [Ni(acac)$_2$·2H$_2$O],[4] and 3.05 A [Ni(acac)$_2$].[43] If the difference in coordination configuration is ignored, as in Figure 3, the acac bite distance of 2.584 A obtained by extrapolation of r/Q to 0 in Figure 3 is in fair agreement with the salicylic acid bite distance of 2.620 A around the hydrogen ion.[38]

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Characterization and Electronic Structures of Six-Coordinate Trigonal-Prismatic Complexes

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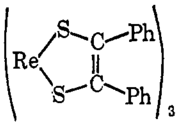
Abstract: The physical properties of the tris(*cis*-stilbenedithiolato) complexes of Mo, W, and Re are described in detail. The three neutral M(S$_2$C$_2$Ph$_2$)$_3$ complexes exhibit MS$_6$ trigonal-prismatic coordination in the solid state and in solution. The V and Cr complexes in this series are isomorphous with the Mo complex and thus very probably are also trigonal prismatic in the solid state. The syntheses and properties of the tris(toluene-3,4-dithiolato) and tris(benzene-1,2-dithiolato) complexes of Mo, W, and Re are reported. In particular, those properties which have been found to be characteristic of trigonal-prismatic coordination are discussed in detail. It is concluded that at least 12 different well-authenticated complexes, spanning five metals and four different ligands, exhibit a six-coordinate trigonal-prismatic structure. In addition, the existence of numerous other complexes, related to the above by reversible one-electron transfers, is established by polarography. The electronic spectra of all the neutral complexes are discussed in terms of a molecular orbital model of energy levels. The molecular orbital bonding scheme is found to be consistent with the considerable electronic spectral and polarographic data.

Six-coordinate complexes of bidentate, unsaturated sulfur-donor ligands have been the subject of extensive current investigations.[2–7] These studies have recently assumed a new and quite fundamental significance in transition metal chemistry. The structure of Re(S$_2$C$_2$Ph$_2$)$_3$ (I) has been solved by X-ray diffraction analysis[8] and has been found to contain a near-perfect trigonal-prismatic array of sulfur-donor atoms. In addition, this first exception[9] to the maxim "six-coordination equals octahedral complex" has been shown not to stand alone. Thus, we have presented evidence that the complexes W(S$_2$C$_2$Ph$_2$)$_3$[8,10] and Re(tdt)$_3$[10] (II) also have trigonal-prismatic structures.



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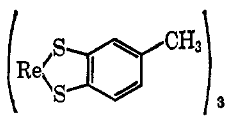

Re(tdt)$_3$

II

In addition, a very recent X-ray study by Smith and co-workers has shown that the Mo(S$_2$C$_2$H$_2$)$_3$ complex is trigonal prismatic.[11] Furthermore, I has been shown to retain trigonal-prismatic coordination in liquid solutions.[10]

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(9) This is the first reported trigonal-prismatic molecular complex. Trigonal-prismatic coordination was first reported [R. G. Dickinson and L. Pauling, *J. Am. Chem. Soc.*, **45**, 1466 (1923)] for the infinitely extended lattices of molybdenite (MoS$_2$) and tungstite (WS$_2$). These are not molecular complexes and, although some of the factors stabilizing these systems and the molecular trigonal prisms discussed above may be similar, it is also probable that other factors such as metal–metal interaction and crystal packing requirements are effective in stabilizing trigonal-prismatic coordination in MoS$_2$ and WS$_2$.

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