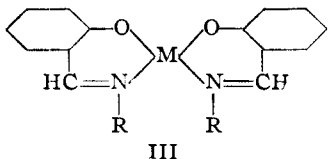
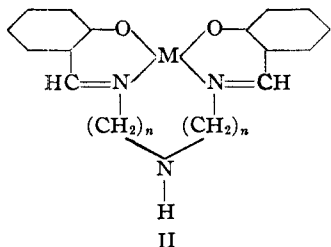
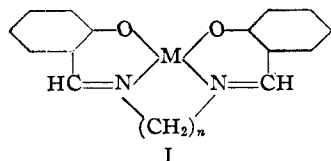


[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Oxygen-carrying Synthetic Chelate Compounds. IV. Magnetic Properties¹BY M. CALVIN AND C. H. BARKELEW^{1a}

In connection with the investigation of the oxygen-carriers, we have studied the magnetic susceptibility of a number of transition group chelates. The measurements may be grouped into three classes, which will be discussed separately: A, susceptibilities at room temperature; B, temperature dependence; and C, susceptibility as a function of fraction oxygenation.

The chelates fall into three general types



Two cases were of especial interest, and will be referred to so frequently that abbreviations were adopted.

	Abbreviations	
Case I $n = 2$	Sal-En	
Case II $n = 3$	Sal-prtr	

Included also are derivatives of salicylaldehyde itself, crystalline solvates of a number of compounds represented by the above structures, plus a small number of compounds not included with above generalization.

The compounds were synthesized by well-known techniques, described by Pfeiffer^{1b}; preparation of new compounds will be discussed in a paper soon to be published,² and their preparations will not

(1) The work herein reported was carried out in part under a Contract (OEMsr-279) between the National Defense Research Committee and the University of California.

(1a) Present address: Shell Development Co., San Francisco, Calif.

(1b) P. Pfeiffer and co-workers, *Ann.*, **503**, 84 (1933); *J. prakt. Chem.*, **140**, 29 (1934); **145**, 243 (1936); **149**, 217 (1937); **150**, 261 (1938); **152**, 145 (1939); **153**, 265 (1939); **155**, 77 (1940); *Angew. Chem.*, **53**, 93 (1940).

(2) R. H. Bailes and M. Calvin.

be described at this point. Earlier workers^{3,4,5} have prepared and measured the susceptibilities of a few of these and similar compounds. Our results for the same compounds are in substantial agreement, with a single exception.

The susceptibilities were measured using a Gouy balance. The samples were ground in an agate mortar and packed uniformly into a calibrated cylindrical glass tube. The force exerted by a magnetic field on the tube was found with a balance capable of weighing to 0.02 mg. The field was calibrated at several current strengths with distilled water, and twice recrystallized copper sulfate pentahydrate. Fields of 5,000 to 12,000 gauss were used, and each sample was measured in at least three field strengths, to detect and correct for any ferromagnetic impurities.

In a number of cases, principally among the iron compounds, it was necessary to fill the tubes in an inert atmosphere to prevent oxidation.

The following tables, arranged by metal, give the susceptibilities measured in this Laboratory. All values are molal susceptibility at 25°, unless otherwise stated, and include Pascal's correction for the diamagnetism of the molecule.

TABLE I

COPPER-SALICYLALDEHYDE CHELATES, M = Cu		
Compound	Formula	$\chi_m \times 10^4$
Copper salicylaldehyde		1440
Ethylenediimine	I, $n = 2$	1725
Pentamethylenediimine	I, $n = 5$	1410
Hexamethylenediimine	I, $n = 6$	1390
Heptamethylenediimine	I, $n = 7$	1070
Anil	III, R =	1410
4-NO ₂ Anil	III, R =	1770
4-OH Anil	III, R =	950
4-CH ₃ Anil	III, R =	1360
4-COOH Anil	III, R =	1310
4-NaSO ₃ Anil	III, R =	1670
4-Phenyl Anil	III, R =	1350
4-Methoxy Anil	III, R =	1220

(3) Tyson and Adams, *THIS JOURNAL*, **64**, 181 (1942).

(4) Klemm and Raddatz, *Z. anorg. Chem.*, **250**, 207 (1942).

(5) D. P. Mellor and co-workers, *J. Proc. Royal Soc. New South Wales*, **74**, 129 (1940); **74**, 475 (1941); **75**, 27 (1941); *THIS JOURNAL*, **64**, 181 (1942).

TABLE I (Concluded)


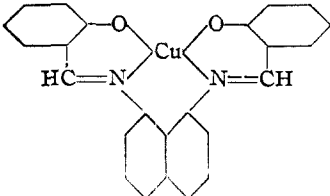
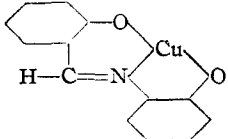
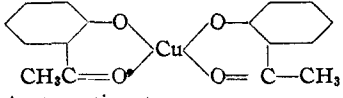
Compound	Formula	$\chi_m \times 10^6$
Benzylimine	III, R = $-\text{CH}_2-$ 	1360
Imine	III, R = H	1500
Ethanolimine	III, R = $-\text{CH}_2\text{CH}_2\text{OH}$	1280
Heptylimine	III, R = $-(\text{CH}_2)_6\text{CH}_3$	1390
Aldoxime	III, R = $-\text{OH}$	1350
Triamine	II, $n = 3$	810

TABLE II

COPPER CHELATES NOT FALLING INTO THE ABOVE CLASSES

Compound	$\chi_m \times 10^6$
	1010
	1040
	1085
Acetoacetic ester	1390
Trifluoroacetylacetone, two forms	gray 1750 blue 1340

For a single unpaired spin, one expects a value of 1280×10^{-6} . Higher values are caused by incomplete quenching of the orbital contribution to the magnetic moment. Lower values are attributed to impurities.

TABLE III

FERROUS SALICYLALDEHYDE CHELATES

Compound	Formula	$\chi_m \times 10^{-4}$
En + $\frac{1}{2}$ En (solvation)	I, $n = 2$	10,850
3-Methoxy Sal En	I, $n = 2$, 3-OCH ₃	10,600
Diethylene triamine	II, $n = 2$	16,200
3-Methoxy Sal prtr.	II, $n = 3$, 3-OCH ₃	15,000
3-Chloro Sal prtr.	II, $n = 3$, 3-Cl	10,300
3-Ethoxy Sal prtr.	II, $n = 3$, 3-OC ₂ H ₅	11,000

The value to be expected for four unpaired spins is $10,000 \times 10^{-6}$. The values quoted are subject to an uncertainty estimated to be ± 1000 , because of the extreme difficulty in preventing atmospheric oxidation. However, they unquestionably indicate four unpaired electrons for all compounds.

TABLE IV

NICKEL SALICYLALDEHYDE COMPOUNDS

Compound	Formula	$\chi_m \times 10^4$
Sal prtr	II, $n = 3$	4450
3-Methoxy Sal prtr	II, $n = 3$, 3-OC ₂ H ₅	4260
Sal En	I, $n = 2$	0

A complete discussion of nickel compounds is to appear soon. It will include three series of type

I, with discussion of color, water of solvation, and methods of preparation. Susceptibilities measured in connection with this work will not be presented here.

For two unpaired spins, a value of $\chi_m = 3350 \times 10^{-6}$ is expected.

TABLE V

COBALT SALICYLALDEHYDE COMPOUNDS^a

(a) Sal En forms	Type I, $n = 2$ $\chi_m \times 10^6$
Inactive	2170
Active	2650
Pyridinate	1900
Peroxide	~200
Pyridine-peroxide	50
(b) 3 Fluoro Sal En forms	Type I, $n = 2$ 3-F
Inactive	2750
Brown hydrate	5170
Red hydrate	1950
Piperidinate	4360
Hydrate-peroxide	0
Active	2740
(c) 3 Ethoxy Sal En	Type I, $n = 2$ 3-OC ₂ H ₅
Pyridinate	4500
Red hydrate	3460
Yellow hydrate	8800
Active	2680
(d) Other cobalt Sal En compounds	$\chi_m \times 10^6$
3-Methoxy hydrate	8530
3-Methoxy	2500
3-Allyl	1980
3-Ethyl	2500
6-Methoxy	2340
3-Butoxy hydrate	9700
5-Fluoro	1960
4-Methoxy hydrate	8850
3-Chloro	3740
5-Methyl hydrate	2740
5-Methyl	3100
3-Phenyl	7890
3-Chloro, 5- <i>t</i> -butyl	3300
(e) Cobalt Sal prtr compounds	II, $n = 3$
Co Sal prtr	7700
Co Sal prtr hydrate	7840
Co Sal prtr peroxide	1200
3-Nitro	6960
3-Chloro	8000
3-Methoxy	8950
3-Ethyl-4 methoxy	6500
4-Nitro	8020
6-Chloro	7780
3-Methyl	8850
3-Methoxy hydrate	8060
3-Phenyl	8430
5-Methyl	7070
5-Chloro	7700
5-Hydroxy	7880
4-Methoxy	8790
3-Fluoro	7420
3-Ethyl	8600

TABLE V (Concluded)
(f) Other cobalt salicylaldehyde chelates

Compound	Formula	$\chi_m \times 10^3$
<i>cis</i> -Cyclohexone-diimine ^b		2405
<i>trans</i> -Cyclohexone-diimine ^b		2390
N-Methyl prtr ^b	II, $n = 3$, methyl on lower N	8750
Diethylene triamine	II, $n = 2$	2030
	(<i>trans</i>) ^b	2610
		3360
		2380

^a A complete description of all forms of the oxygen-carriers is to be found in another paper of this series, Calvin, Bailes and Wilmarth, *THIS JOURNAL*, **68**, 2254 (1946); Bailes and Calvin, forthcoming. ^b The diamines in these compounds were prepared for us under the direction of Dr. T. A. Geissman at U. C. L. A.

The values expected are: 1 unpaired spin, 1280; 3 unpaired spins, 6280.

Discussion of Results

Copper Compounds.—We expect a single unpaired electron for copper compounds, irrespective of the type of linkage or of the structure of the molecule. Cupric ion, covalently bound copper with square dsp^2 hybridization, or tetrahedral sp^3 hybridization, all have a single unpaired electron. The fact that the values are so close to that predicted for spin only indicates that the orbital contribution is almost completely quenched by the crystalline fields. As yet, no significant conclusion concerning molecular structure can be drawn from these data.

Iron Compounds.—All ferrous compounds have four unpaired electrons, which indicates strongly that iron is present in the ionic state, in view of the fact that similar cobalt and nickel compounds will be shown to be planar. Covalent

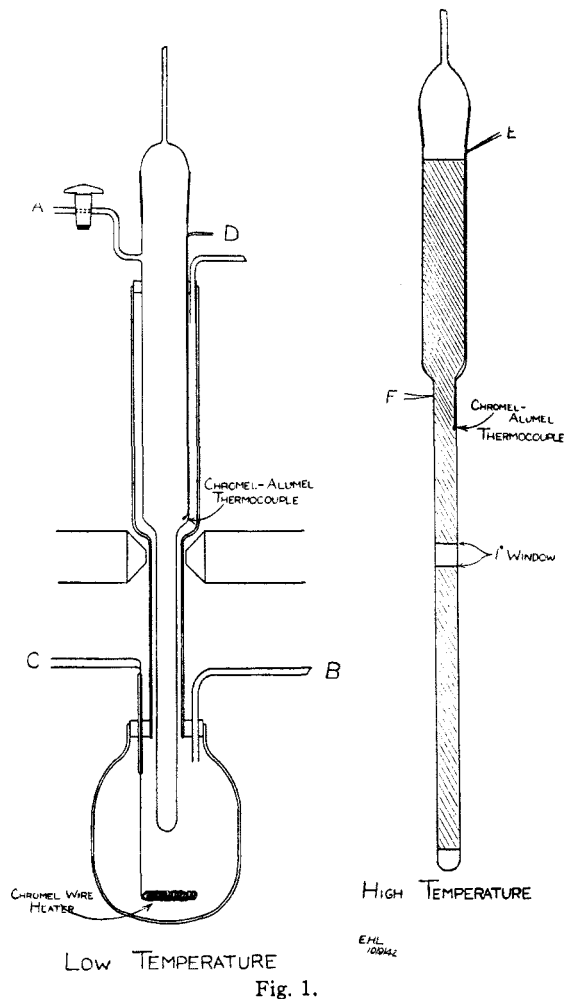


Fig. 1.

iron with planar dsp^2 hybridization would have two unpaired spins. The rather high orbital contribution in most cases shows little quenching effect. The two anomalously high values recorded in Table III might conceivably be due to the presence of some ferric iron although qualitative tests indicate its virtual absence. Ordinary ultimate analysis would not indicate its presence.

Nickel Compounds.—Nickel salicylaldehyde ethylenediimine is shown to be planar from its diamagnetism, whereas the others are either ionic or tetrahedral. A more complete discussion of nickel compounds is to follow in a later paper.

Cobalt Compounds.—It has been hoped that some magnetic criterion of oxygen-carrying activity would make itself apparent; however, the above results indicate that this is not the case, at least for the compounds in the solid state. It appears, however, that a necessary though not sufficient condition is that the 2-1 compounds have one unpaired electron, while the 1-1 compounds have three unpaired electrons.

The ethylenediimine chelates are for the most part covalent square planar, with a single unpaired electron, the single exception being the 3-phenyl

TABLE VI

T, °K.	$\chi_m \times 10^6$	T, °K.	$\chi_m \times 10^6$	
CLASS I: COMPOUNDS WHICH OBEY THE CURIE-WEISS LAW				
Copper salicylaldehyde ethylenediimine (Fig. 2)		Cobalt salicylaldehyde "prtr" hydrate (Fig. 7)		
94	4870	96	23,500	
162	3015	120	19,600	
226	2170	140	15,880	
250	1980	166	13,700	
274	1820	187	12,650	
294	1725	208	10,880	
320	1580	228	10,100	
345	1480	250	9250	
370	1380	270	8550	
Copper salicylaldehyde methylimine (Fig. 3)		Cobalt salicylaldehyde "prtr" active (Fig. 8)		
96	3950	96	23,200	
164	2540	120	18,450	
250	1695	140	61,100	
300	1432	166	13,700	
320	1350	188	12,080	
345	1260	208	10,870	
370	1180	228	9950	
400	1090	250	9000	
Active cobalt salicylaldehyde ethylene diimine (Fig. 4)		270		8400
100	6100	293	7670	
124	5450	320	7060	
160	4460	345	6640	
212	3600	370	6170	
240	3220	400	5720	
CLASS II: COMPOUNDS WHICH DO NOT OBEY THE CURIE-WEISS LAW				
Cobalt 3-methoxysalicylaldehyde ethylenediimine hydrate (Fig. 5)		Cobalt 3 ethoxy salicylaldehyde ethylenediimine red hydrate (Fig. 9)		
100	21,300	96	5100	
164	13,900	120	4560	
200	11,830	140	4200	
220	11,040	168	3840	
252	9800	187	3500	
296	8530	208	3460	
Cobalt 3-methoxy salicylaldehyde ethylenediimine active (Fig. 6)		227		3470
96	7560	250	3450	
120	6020	270	3460	
140	5380	293	3460	
164	4580	Cobalt salicylaldehyde ethylenediimine pyridinate (Fig. 10)		
188	4130	98	5180	
208	3600	128	3360	
228	3220	150	2910	
		170	2580	
		180	2470	
		196	2370	
		220	2370	

250	2360	188	2670
272	2270	216	2520
295	1900	228	2500
Cobalt salicylaldehyde ethylenediimine, inactive isomer (Fig. 11)		248	2480
		268	2390
		282	2210
		290	2170
102	4460	320	2130
112	4030	345	2130
126	3570	370	2130
137	3330	400	2130
151	3030		

in which steric effects are acting to prevent a planar structure. A number of hydrates show 3 unpaired spins, probably indicating ionic cobalt, while a few show intermediate values. These latter will be discussed in the section on temperature dependence.

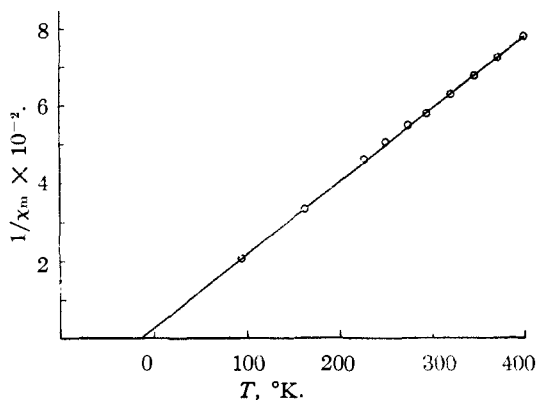


Fig. 2.—Copper salicylaldehyde ethylenediimine.

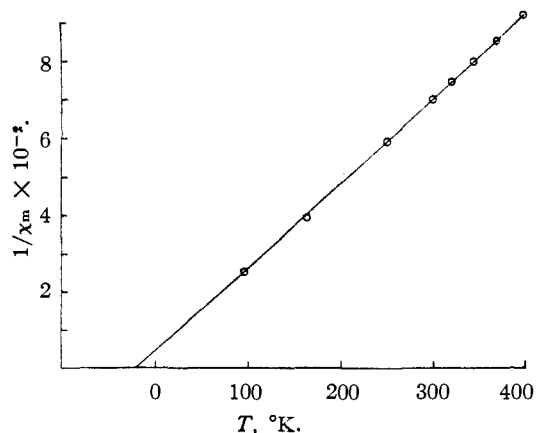


Fig. 3.—Copper salicylaldehyde methylimine.

The value of three unpaired spins for the prtr compounds is evidence that this cobalt is ionic, since chemical evidence shows the cobalt to be 5-coordinated, in a tetragonal pyramidal configuration. The ease of crystal formation, something which is not found in compounds in which the nitrogen is replaced by carbon, indicates a compact and rigid molecular structure, while the oxygen-carrying capacity indicates an open sector in

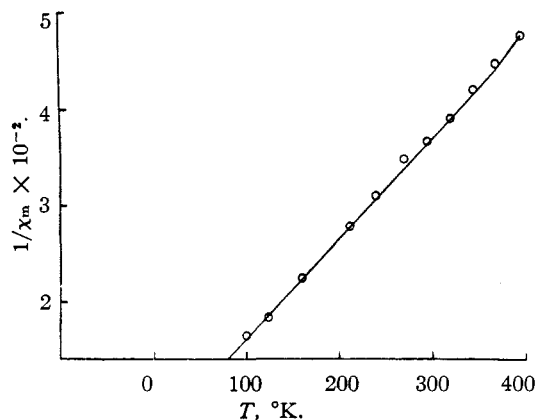
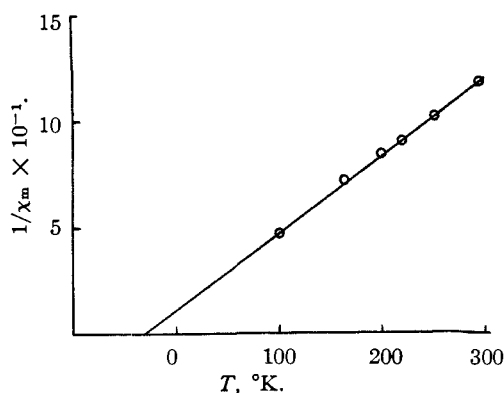
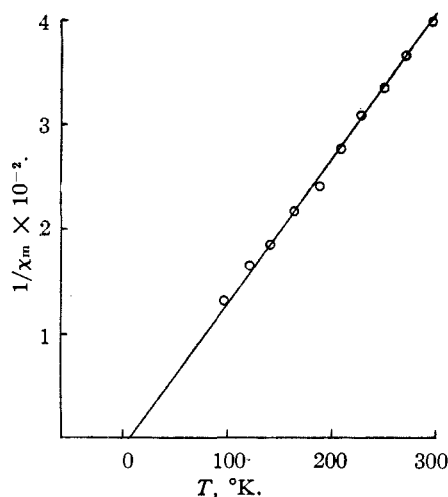


Fig. 4.—Cobalt salicylaethylenediimine active.

Fig. 5.—Co₃MeOSalEn hydrate.Fig. 6.—Co₃MeOSalEn active.

the coordination sphere. The covalent hybridizations leading to a tetragonal pyramid are d^2sp^2 , d^4s , d^2p^3 , d^4p , all of which would have one unpaired electron.⁶

It was found, without exception, that all red or brown compounds are planar, and all yellow, yellow green, or orange compounds are tetrahedral or ionic. This generalization was first pointed out

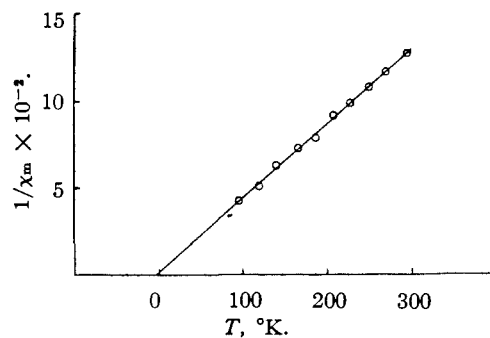
(6) Kimball, *J. Chem. Phys.*, **8**, 128 (1940)

Fig. 7.—CoSal Prtr hydrate.

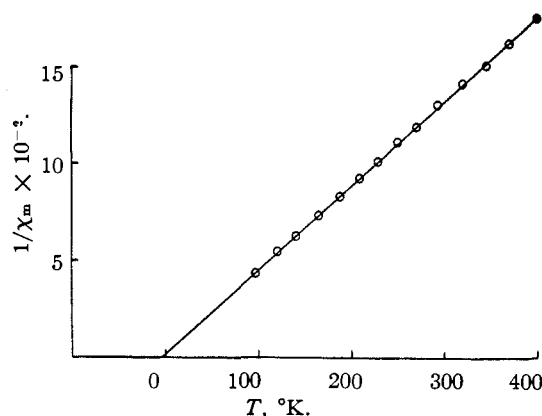
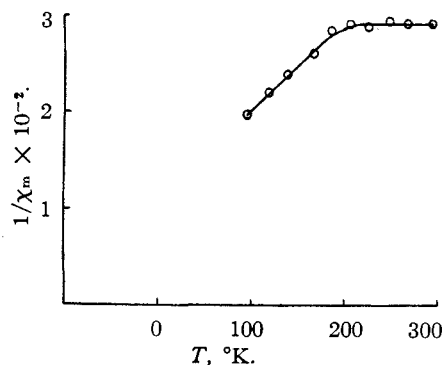


Fig. 8.—CoSal Prtr active.

Fig. 9.—Co₃EtOSalEn red hydrate.

by Mellor.⁵ It is the measurement of CoSal En which differs from that of Mellor. He apparently had peroxide formation, probably being unaware of the compound's oxygen activity.

Temperature Variation of Susceptibility

The apparatus for temperature control is shown in Fig. 1. The sample was suspended inside the central vessel, past which a stream of constant temperature air was rapidly blown. The stream of air was produced by boiling liquid air; its temperature was controlled to $\pm 0.5^\circ$ by its rate of boiling and the liquid level in the boiler. The latter was held constant by intermittent addition of liquid air; the current through the heater was controlled with a rheostat. The operation was

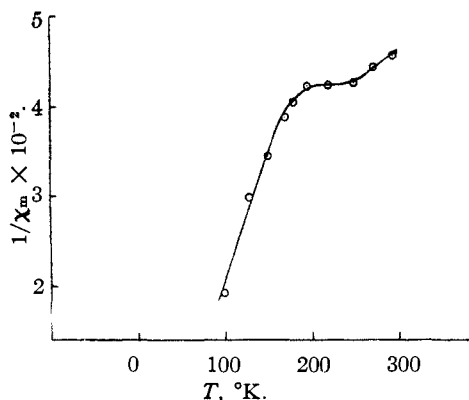


Fig. 10.—Cobalt salicylaethylenediimine pyridinate.

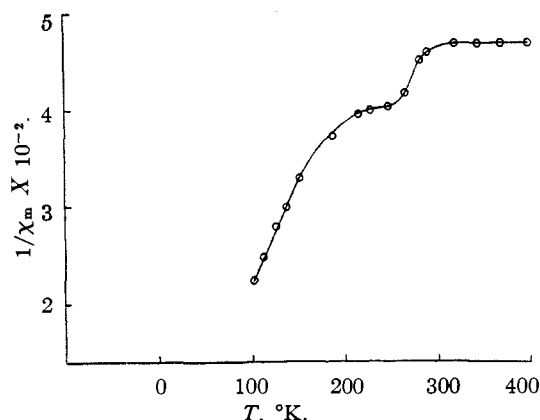


Fig. 11.—Cobalt salicylaethylenediimine inactive.

completely automatic; the thermocouple controlled a system of magnetic valves which operated the liquid air stream. Each sample was allowed one hour to reach temperature equilibrium before measurement.

Temperatures above 25° were attained with a simple non-inductive furnace. The current through the heater was controlled by a thermocouple.

The compounds measured fell into two general classes, according to whether or not they obeyed the Curie-Weiss law

$$\chi_m = B^2 \mu^2 / 3k(T - \theta)$$

This predicts that the reciprocal molal paramagnetic susceptibility will be linear with temperature, with slope inversely proportional to the square of the magnetic moment. In the above formula, β and k are universal constants, μ is the moment, and θ is a characteristic constant.

Discussion

The first eight compounds described, those in class I, appear to obey the Curie-Weiss law closely, and, for this reason, they merit little comment. The compounds in class II, three cobalt chelates, show an unusual and quite characteristic deviation. The susceptibility shows a plateau in the intermediate temperature region,

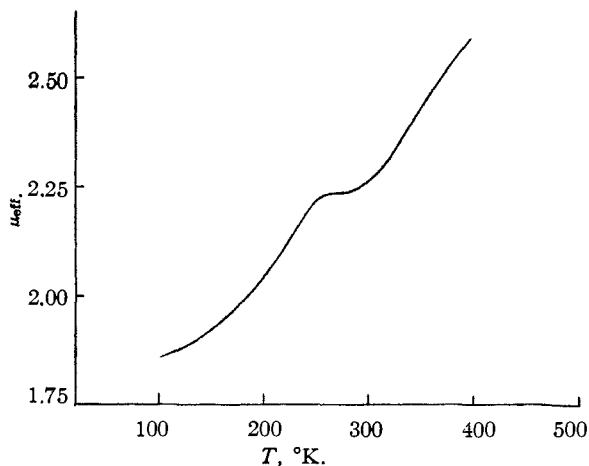
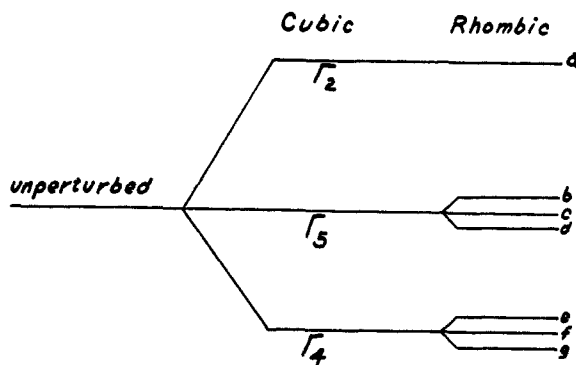


Fig. 12.—Cobalt salicylaethylenediimine inactive.

indicating that the moment is decreasing. For convenience, we have plotted $\mu_{\text{eff.}} = 2.83 \sqrt{\chi_m T}$ against T in Fig. 12. No crystal transitions have been observed for these compounds at these temperatures, so the conclusion drawn is that the behavior is due to a loss in magnetic entropy of the cobalt atom. This implies splitting of the degenerate orbital levels by the crystalline field in such a manner as to give rise to the phenomenon. Bethe⁷ has shown that crystalline fields split the levels as diagrammed in Fig. 13, and it has further

Fig. 13.—Co²⁺.

been demonstrated by Van Vleck,⁸ that the high anisotropy of most cobalt compounds is a corollary of the same effect. It is clear that such a splitting, assuming the crystalline symmetry to be rhombic or of a lower order, can account for the behavior observed, if the plateau in the moment occurs between the levels marked d and e. For compounds in which the splitting is not so wide, those in case I, or compounds which do not split with an almost degenerate lower level, such as copper compounds, the effect is not observed.

The Change in Magnetism on Oxygenation

Two samples, one of cobalt salicylaldehyde ethylenediimine, and one of cobalt salicylaldehyde

(7) Bethe, *Ann. Phys.*, **3**, 133 (1929).

(8) Van Vleck, *Phys. Rev.*, **41**, 208 (1932).

"prtr," were oxygenated in stages and the magnetic susceptibility at each stage measured. The oxygenations were carried out by suspending the weighed, filled tubes in a bomb and exposing to oxygen for various intervals of time. The extent of oxygenation was determined by weight.

The sample of the parent diamine showed the following behavior when exposed to 1 atmosphere of oxygen.

Time, min.	% O ₂	$\chi_m \times 10^6$
0	0.0	2490
2	0.21	2440
3	0.62	2290
15	1.44	1862
20	1.85	1550
30	3.11	990
50	4.34	476
	4.90 (complete)	160

The data are plotted in Fig. 14. The line is straight, showing simple additivity of susceptibilities, as would be expected for a two-phase solid system.

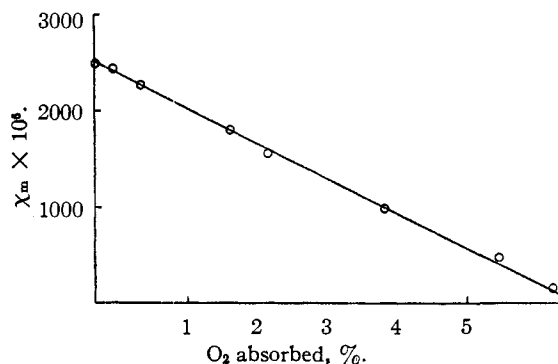


Fig. 14.—CoSalEn.

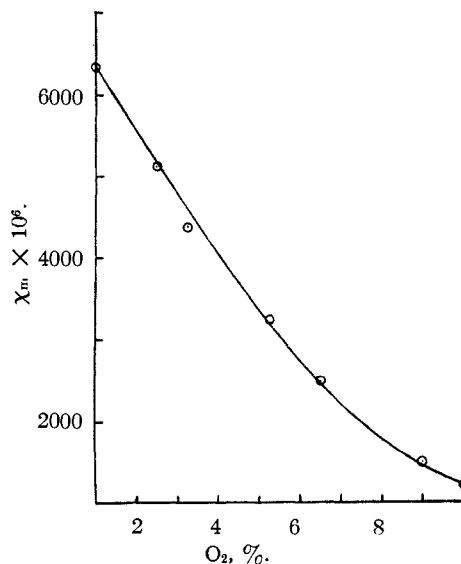


Fig. 15.—CoSal Prtr.

A similar plot of the parent triamine is shown in Fig. 15. The curvature of the line may be due to non-additivity of the components. It is also consistent with the possibility that irreversible oxidation is taking place as saturation is approached. Cobaltic compounds would be expected to have 2 or 4 unpaired spins, in any case more than the one for the peroxide.

Summary

Room temperature susceptibilities of a number of transition element chelates have been measured.

The variation of susceptibility with temperature has been studied, and characteristic anomalies discussed with respect to crystal symmetry.

Susceptibility as a function of oxygenation has been studied for two oxygen carriers.

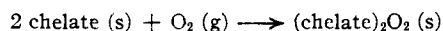
RECEIVED APRIL 8, 1946

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA, AND THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY¹]

The Oxygen-carrying Synthetic Chelate Compounds. V. Equilibrium with the Solid Compounds^{1a}

BY E. W. HUGHES,² W. K. WILMARTH³ AND M. CALVIN

The present work is concerned with the measurement of the equilibrium represented by the general reaction



where the chelates are of type I⁴ and bearing

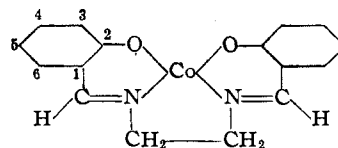
(1) No. 1065.

(1a) The work herein reported was done under a Contract (OEM-sr-279) between the National Defense Research Committee and the University of California.

(2) Present address: California Institute of Technology, Pasadena.

(3) Present address: University of Southern California, Los Angeles.

(4) Calvin, Bailes and Wilmarth, *THIS JOURNAL*, **68**, 2254 (1946).



various substituents in the benzene ring.⁵

Both the oxygen equilibrium pressure and the X-ray powder diagrams of the solid phase were taken as a function of the oxygen content of the solid phase.

(5) We will use the abbreviation CoSaEn for this type, inserting the substituents as required.