

complexes. The transition dipoles, μ_{mn} , and f -values presented in Table IV are estimated from the reported values of ϵ_{\max} and $\Delta\nu_{1/2}$, the half-intensity width ($\Delta\nu_{1/2}$ is usually estimated from figures presenting spectra in the references cited) using the approximation: $\int \epsilon d\nu = \epsilon \Delta\nu_{1/2}$. This estimate is probably low (see Briegleb⁹), but we do not believe the data are good enough to warrant refinements.

TABLE IV
COMPARISON OF THE PROPERTIES OF ANTHRACENE-I₂ AND PHENANTHRENE-I₂ COMPLEXES WITH OTHER RELATED I₂ COMPLEXES

Donor	K_{25}°	$-\Delta H_f$		λ_{CT} , m μ	ϵ	$\Delta\nu_{1/2}$, cm. ⁻¹	μ_{mn}^a Debyes/ Å.
		kcal./ mole	m μ				
Benzene ^b	0.15	1.3	292	15,000	5100	4.6	
<i>o</i> -Xylene ^b	.27	2.0	318	11,000	(5000) ^c	(4.0) ^c	
Durene ^b	.63	2.8	332	9,000	(5000) ^c	(3.7) ^c	
Naphthalene ^b	.25	1.8	360	7,400	4700	3.4 ^d	
Phenanthrene	.45	1.6	364	7,100	4900	3.4	
Anthracene	3.0 ^e	...	<430	(550) ^e	(5000) ^c	(>1.0) ^{c,e}	

^a Approximate transition dipole for the charge-transfer absorption, defined by $\mu_{mn}^2 = 0.0092 \int \epsilon d\nu / \nu_{\max}$; the integral is approximated by $\epsilon_{\max} \Delta\nu_{1/2}$. ^b Values from Briegleb, ref. 9, except for μ_{mn} and $\Delta\nu_{1/2}$, which were estimated from figures in the original papers cited by Briegleb, or else guessed. ^c These values are "educated guesses" and should not be used for more than order-of-magnitude estimates. ^d This value is to be compared with a value of $\mu_{mn} = 4.0$ D./Å. computed from the f -values obtained by actual numerical integration of ϵ ; see N. W. Blake, H. Winston, and J. A. Patterson, *J. Am. Chem. Soc.*, **73**, 4437 (1951). ^e The product of K and ϵ is believed to be correct, but each could be in error. *I.e.*, K could be as low as 0.3 and ϵ as high as 5500. Furthermore, the maximum in the charge-transfer absorption may not be at 430 m μ .

The comparison in Table IV suggests that the intensities of the charge transfer bands for I₂ complexes with polynuclear aromatic compounds may decrease somewhat as the strength of the complex increases. However, the magnitude of the change is much smaller than reported earlier⁴ and discussed by Murrell.⁵ Especially for anthracene-I₂, it seems very likely that

the charge transfer maximum is at longer wave lengths and more intense than reported here.

Finally, we note that the strength of the complexes between aromatic donors and I₂ does increase in the order: benzene < naphthalene < phenanthrene < anthracene (see Table IV). However, instead of an increase in K by a factor of 50 from phenanthrene to anthracene,⁴ we now find a change by only a factor of 7. This increase in base strength is still sizable, and, *if real*, is apparently due to the increase in resonance stabilization (X_0) of the ground state of the complex. Some increase should be expected because the lower ionization potential of anthracene causes the energy of the dative state (W_1) to be less, so that the resonance interaction with the ground state is greater.

It has been suggested elsewhere^{9,18} that the resonance energy of these weak complexes of I₂ with aromatic donors can be calculated from the perturbation equation

$$X_0 = -\beta_0^2 / (W_1 - W_0) = -0.36 / (I_D - 5.2) \text{ e.v.}$$

For phenanthrene-I₂, $X_0 = -0.12$ e.v. = -2.8 kcal./mole; for anthracene-I₂, $X_0 = -0.14$ e.v. = -3.2 kcal./mole.¹⁹ As shown earlier,¹⁸ the energy of formation of these complexes should approximately equal X_0 , in agreement with these results. However, this estimate of ΔH_f suggests that the difference between the K 's for phenanthrene and anthracene complexes in Table IV is still too large, and that our value for the anthracene complex may still be too high.

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(18) W. B. Person, *J. Chem. Phys.*, **38**, 109 (1963); R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

(19) These values are obtained using calculated ionization potentials of 8.1 and 7.7 for phenanthrene and anthracene, respectively.

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The Stereochemistry of Metal Chelates with Multidentate Ligands. II

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Complexes of bis-salicylaldehyde-triethylenetetramine with manganese(III), cobalt(II), nickel(II), indium(III), and gallium(III) have been prepared. Their structures, as indicated by their spectra in the infrared, are discussed.

In view of the stereochemical properties of the chelating agent, bis-salicylaldehyde-triethylenetetramine $\text{HOC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{OH}$ (I), described in part I,¹ it was considered worthwhile to prepare and study compounds with a series of metals. Two different methods have been used to synthesize these compounds. In one method, tris-(salicylidene-amino)-triethylenetetramine is formed by mixing salicylaldehyde and triethylenetetramine. When a metal ion is introduced, 1 mole of salicylaldehyde is cleaved and a metal complex of I is formed. In the second method, a metal complex of salicylaldehyde is allowed to react with triethylenetetramine to form the complex of I.

Crystalline complexes of I with manganese(III), cobalt(II), nickel(II), indium(III), and gallium(III) have been isolated and purified. Attempts to isolate pure compounds of iron(II), palladium(II), platinum(II), cadmium(II), zinc(II), and rhodium(III) were unsuccessful.

It was reported previously¹ that the complexes of iron(III), copper(II), aluminum(III), and cobalt(III) possess sufficient solvolytic stability to be resolved into their optical isomers. Magnetic measurements showed the iron(III) complex to be a spin-paired d^2sp^3 compound. In the present work, however, the manganese(III), nickel(II), and cobalt(II) complexes were found to be spin-free, with magnetic moments of 5.05, 2.88, and 4.12 B.M., respectively.²

(2) The moment for the cobalt(II) complex is a little lower and for manganese(III) is slightly higher than ordinarily expected. The reason for this

(1) B. Das Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **77**, 5476 (1955).

Dodson and Hall³ have recently studied several crystalline modifications of the nickel(II) complex. In all cases the complexes were paramagnetic, with magnetic moments ranging from 3.0 to 3.15 B.M.

An attempt was made to resolve the manganese(III) complex by the method which was used successfully in resolving the iron(III) and aluminum complexes. However, on fractionation of the antimonyl *d*-tartrate salt of the manganese complex, no isomer separation was observed.

The results of the magnetic measurements on the cobalt(II) complex were of special interest because they differed from those obtained previously for the cobalt(II) compound synthesized by a different method.¹ This led to a re-examination of the earlier prepared complex which possessed an apparent magnetic moment of 2.01 B.M. and was originally believed to be spin paired. The synthesis was repeated under identical conditions with one important exception. During the complete operation, precautions were taken to exclude oxygen rigorously. The synthesis was performed in a gloved box under nitrogen, and the solutions were deoxygenated before use. The product was dried rapidly at room temperature *in vacuo*. The magnetic moment was 4.11 B.M., which is in good agreement with that obtained for the complex prepared by the reaction of tris-(salicylideneamino)-triethylenetetramine with cobalt(II). Apparently the credible but erroneous value obtained previously arose from partial oxidation of the complex to a cobalt(III) or a peroxo species. Other workers⁴ have observed that several Schiff base complexes of cobalt(II) readily undergo oxidation. For some reason which is not immediately obvious, the complex prepared by the reaction of tris-(salicylideneamino)-triethylenetetramine and cobalt(II) does not undergo oxidation as rapidly as that prepared from cobalt(II) salicylaldehyde and triethylenetetramine. The former method requires no elaborate provisions for excluding oxygen and is also simpler. The infrared spectra of the products prepared by the two methods are identical.

The infrared spectra of the complexes were obtained both in potassium bromide disks and in Nujol mulls, and selected bands are shown in Table I. The potassium bromide system did not offer much advantage with this series of compounds. Where the resolution was poor in Nujol, as in the case of the cobalt(III) complex, no better results were obtained in potassium bromide. The absence of Nujol bands (2920, 2860, 1467, 1382 cm^{-1}), however, revealed the $-\text{CH}_2-$ (str.) vibrations, and the aromatic $-\text{C}=\text{C}-$ bands at 1470–1480 cm^{-1} were also apparent. The N–H and O–H stretching bands were shifted a little toward lower frequencies in the potassium bromide disks, but the other bands were practically unaffected.

The three bands around 1125, 1150, and 1200 cm^{-1} are possibly associated with the stretching vibrations of $-\text{C}-\text{N}-$ in the system $-\text{C}-\text{N}-\text{C}-\text{C}-\text{N}-\text{C}-$ and have been recorded in the order of their decreasing intensities.

As pointed out in part I, several bands in the 3000–3700 cm^{-1} region have been observed for most of the complexes. They undoubtedly are N–H and in some cases O–H stretching bands. The sharpness of these bands leads us to believe that quite a few of them arise from N–H vibrations rather than O–H present in the water of crystallization, as the latter are observed generally as broad bands. The explanation of the multiple

is not apparent, but it is possible that the samples were contaminated with small amounts of cobalt(III) and manganese(II), in spite of elaborate precautions (*vide infra*) in the case of the cobalt(II) complex to avoid this.

(3) G. G. Dodson and D. Hall, *J. Inorg. Nucl. Chem.*, **23**, 33 (1961).

(4) M. Calvin, R. H. Bailes, and W. K. Wilmarth, *J. Am. Chem. Soc.*, **68**, 2254 (1946).

peaks may be that when the secondary nitrogens are coordinated to a metal, some effect similar to the formation of amine salts is operative to split the N–H stretching frequency into a number of bands. We have observed a similar effect to a less marked degree when a diamine is coordinated to a metal ion. If this be the case, the presence of multiple peaks in this region may indicate that the secondary nitrogens are coordinated to the metal ion.⁵

The spectra of all of the complexes except those of copper(II) and manganese(III) show multiple peaks in the N–H region. It may tentatively be concluded from this that the secondary amine groups are coordinated to the metal in the complexes of cobalt(III), iron(III), aluminum(III), gallium(III), indium(III), nickel(II),⁶ and cobalt(II).

As can be seen from Table I, the $\text{C}=\text{N}$, $\text{C}-\text{N}$, $\text{CH}_2(-\text{N})$, and $\text{C}-\text{O}$ vibrations occur at similar frequencies for all the complexes in spite of the expected wide variation in metal–nitrogen and metal–oxygen bond strength as the metal changes. It is not surprising, however, that differences in bonding as reflected in infrared spectra, in such a complicated ring system with stringent steric requirements (seven fused rings in the sexadentate case) are not as readily predictable as in simpler molecules.

Based on the infrared and magnetic measurements it is concluded that most of the complexes of I are probably octahedral. The copper complex is probably square planar, but the magnetic susceptibility data rule out square planar configurations for the cobalt(II) and nickel(II) complexes.

Experimental

I. Bis-salicylaldehyde-triethylenetetraminemanganese(III) Iodide Hydrate $[\text{Mn}(\text{TS}_2)]\text{I}\cdot\text{H}_2\text{O}$.—To a solution of 19 g. of manganese chloride 4-hydrate in 75 ml. of water was added 24 g. of salicylaldehyde dissolved in 150 ml. of methanol, while the mixture was cooled in ice. A solution of 8 g. of sodium hydroxide in a mixture of 25 ml. of water and 50 ml. of methanol was slowly added with mechanical stirring. Bis-salicylaldehyde-manganese(II) separated as a yellowish brown powder. This was washed with water and then with absolute ethanol, and dried in air.

Six grams of bis-salicylaldehyde-manganese(II) was suspended in 50 ml. of water and 20 ml. of a 14.6% aqueous solution of triethylenetetramine was slowly added to it with stirring. When the addition was complete, a current of air was drawn through the mixture for 12 hr. The solution was filtered, cooled in ice, and 2 ml. of concentrated hydrochloric acid was added to it. To this cold dark brown solution (50 ml.) was added a solution of 20 g. of potassium iodide in 50 ml. of water. The dark solid that separated was dissolved in 100 ml. of methanol. The solution was filtered and 100 ml. of water was added to it. On concentration of the solution, the complex iodide separated. This was further purified by recrystallization from a minimum quantity of water previously heated to 80°, washed with cold water and then with a 1:1 mixture of acetone and ether, and dried under vacuum at 90°.

Anal. Calcd. for $[\text{Mn}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]\text{I}\cdot\text{H}_2\text{O}$: C, 43.63; H, 4.36; N, 10.18; Mn, 9.98. Found: C, 44.01; H, 4.63; N, 9.99; Mn, 9.67.

The compound forms chocolate-brown short prismatic needles, highly soluble in alcohols and much less soluble in water.

The magnetic moment was found to be 5.05 B.M., which indicates that there are probably four unpaired electrons. Attempts to prepare the pure manganese(II) compound were unsuccessful owing to its rapid oxidation.

II. Bis-salicylaldehyde-triethylenetetraminecobalt(II) Hexahydrate $[\text{Co}(\text{TS}_2)]\cdot 6\text{H}_2\text{O}$.—To prepare the cobalt(II) compound, a cold solution of 12 g. salicylaldehyde in 25 ml. of acetone was mixed with a solution of 10 ml. of triethylenetetramine (71.3% aqueous solution) in 25 ml. of acetone. The air in the flask was

(5) Infrared and magnetic susceptibility data are, of course, only indicative, and it would be desirable to substantiate conclusions regarding structure by a complete X-ray study.

(6) In ref. 3 it was reported that only a single peak was observed in the N–H region of the spectra of several different modifications of the nickel(II) complex. Our spectra of the compound synthesized by the method reported herein definitely showed multiple but poorly resolved peaks.

TABLE I

INFRARED ABSORPTION PEAKS FOR METAL COMPLEXES OF BIS-SALICYLALDEHYDE-TRIETHYLENETETRAMINE^a

	Co(III)	Fe(III)	Al(III)	Ga(III)	In(III)	Mn(III)	Cu(II)	Ni(II)	Co(II)
O—H (str.)	3595 (3620)	3600 (3610)	3480 (3485)	3410 (3440)	3360 (3450)	3720 (3710)	3170 (3150) ^b	3600	3350 (3300)
and	3410 (3480)	(3510)	3410 (3430)	3270 (3300)	3200 (3210)			3420 (3420)	3220 (3130)
N—H (str.)	3380 (3408)	3430 (3440)	3300 (3300)	3070 (3090)	3030 (3040)			3300 (3280)	3100
	3320 (3318)	3350 (3380)	3280 (3285)					(3140)	
	3150 (3160)	3145 (3170)	3120 (3120)					(3080)	
	3090 (3100)	3060 (310)	3040					3020 (3030)	
C≡N (str.)	1643 (1643)	1628 (1630)	1628 (1634)	1622 (1625)	1623 (1628)	1617 (1615)	1633 (1637)	1640 (1646)	1635 (1636)
C—N (str.)	1205 (1205)	1205 (1205)	1153 (1156)	1193 (1198)	1156 (1159)	1153 (1153)	1151 (1153)	1190 (1196)	1155 (1152)
	1155 (1155)	1152 (1154)	1207 (1207)	1146 (1153)	1188 (1191)	1205 (1205)	1198 (1187)	1149 (1158)	1203 (1192)
	1131 (1131)	1132 (1132)	1131 (1133)	1127 (1130)	1131 (1134)	1133 (1133)	1130 (1131)	1127 (1130)	1133 (1129)
CH ₂ —(N) (def.)	1454 (1457)	1446 (1450)	1457 (1460)	1440 (1451)	1440 (1455)	1449 (1449)	1470 (1470)	1453 (1455)	1445 (1440)
C—O (str.)	1314 (1314)	1300 (1300)	1315 (1315)	1305 (1318)	1304 (1310)	1306 (1306)	1350 (1350)	1345 (1350)	1345 (1344)
								1328 (1311)	1315 (1315)
CH ₂ (str.)	2900	2900	2905	2880	2910	2900	2899	2890	2890
Aromatic	1600 (1605)	1600 (1602)	1603 (1607)	1590 (1602)	1595 (1606)	1607 (1606)	1603 (1604)	1599 (1603)	1600 (1602)
C=C	1538 (1542)	1540 (1542)	1550 (1553)	1524 (1539)	1531 (1537)	1540 (1538)	1538 (1538)	1538 (1544)	1540 (1535)
	1473 (1475)	1475 (1475)	1480 (1480)	1465 (1465)	1467 (1474)	1473 (1470)	1455 (1475)	1472 (1472)	1465 (1473)
C—H (rock)	766 (762)	755 (755)	767 (743)	755 (748)	765 (763)	768 (768)	760 (758)	760 (756)	763 (757)
	756 (755)			(792)	776 (773)				

^a The numbers (in cm.⁻¹) shown in parentheses were obtained with complexes dispersed in Nujol mulls; those without parentheses were obtained with potassium bromide pellets. The spectra were recorded with a Perkin-Elmer Model 21 double beam spectrophotometer. ^b Broad bands with centers at the indicated frequencies.

replaced by a current of nitrogen. A solution of 4 g. of sodium hydroxide in 10 ml. of cold water was added, and then a solution of 11 g. of cobalt chloride 6-hydrate in 120 ml. of water. The flask was immediately stoppered and shaken vigorously. Beautiful orange-yellow prismatic needles formed. They were filtered rapidly and washed thoroughly with water and then with dry ether, and immediately dried under vacuum. Much larger crystals can be obtained by slow crystallization.

Anal. Calcd. for Co(C₂₀H₂₄N₄O₂)·6H₂O: C, 46.25; H, 6.95; N, 10.79; Co, 11.34. Found: C, 46.43; H, 6.93; N, 11.13; Co, 11.23.

The compound prepared by this method, in contrast with that obtained by the previous method,¹ is oxidized only very slowly. These crystals were found to be highly soluble in alcohols, less so in acetone, and only slightly soluble (with oxidation) in water. The magnetic moment was found to be 4.12 B.M., indicating that the complex has three unpaired electrons.

III. Bis-salicylaldehyde-triethylenetetraminenickel(II) [Ni(TS₂)] was synthesized from bis-salicylaldehyde-nickel(II) and triethylenetetramine. The salicylaldehyde complex was prepared by the method used previously¹ for preparing the cobalt(II) complex.

Four grams of an aqueous solution (71.5%) of triethylenetetramine was added to a suspension of 5.9 g. of bis-salicylaldehyde-nickel(II) in a mixture of 100 ml. of water and 100 ml. of methanol. The resulting solution was concentrated on a hot plate to a volume of 60 ml., and then allowed to cool slowly to room temperature. The beautiful reddish brown crystals which formed were separated by filtration, recrystallized from hot 25% methanol, and air dried. The product was found to be highly soluble in methanol, fairly so in ethanol, and slightly soluble in water.

Anal. Calcd. for Ni(C₂₀H₂₄N₄O₂): C, 58.44; H, 5.88; N, 13.62; Ni, 14.29. Found: C, 58.73; H, 6.27; N, 13.45; Ni, 14.21.

When heated in an evacuated melting point capillary, the compound darkens at 260° and melts with decomposition at 272–273°. The magnetic moment was found to be 2.88 B.M. (two unpaired electrons).

IV. Bis-salicylaldehyde-triethylenetetramineindium(III) Iodide [In(TS₂)]I.—Cold solutions of the following were mixed with stirring in the order given: (a) 4.5 ml. of a 20% solution of triethylenetetramine in 20 ml. of ethanol, (b) 1.5 g. of salicylaldehyde in 20 ml. of methanol, (c) 0.7 g. of potassium hydroxide in 5 ml. of water, (d) 1.32 g. of indium chloride in 10 ml. of water containing a drop of hydrochloric acid.

The mixture was kept in an ice bath and stirred for 1 hr. and then filtered. To the filtrate was added a saturated solution of potassium iodide. The solution was allowed to evaporate at room temperature, whereupon the complex iodide crystallized. The product was recrystallized from warm water containing a trace of potassium iodide.

Anal. Calcd. for [In(C₂₀H₂₄O₂N₄)]I: C, 40.44; H, 4.07; N, 9.43; In, 19.33. Found: C, 40.37; H, 4.05; N, 9.46; In, 18.97.

V. Bis-salicylaldehyde-triethylenetetraminegallium(III) Iodide Hemihydrate. [Ga(TS₂)]I·0.5H₂O.—Cold solutions of the following were mixed with stirring in the order given: (a) 14.6 ml. of a 20% solution of triethylenetetramine mixed with 20 ml. of ethanol, (b) 4.9 g. of salicylaldehyde in 40 ml. of ethanol, (c) 2.3 g. of potassium hydroxide in 10 ml. of water, (d) 2.5 g. of gallium chloride in 20 ml. of water containing a drop of hydrochloric acid.

The mixture, cooled in ice, was stirred for 1 hr. The solution was filtered and to the filtrate was added a saturated solution of potassium iodide. The solution was concentrated by slow evaporation and the product which separated was recrystallized from warm water containing a little potassium iodide.

Anal. Calcd. for [Ga(C₂₀H₂₄O₂N₄)]I·0.5H₂O: C, 43.03; H, 4.48; N, 10.04; Ga, 12.50; I, 22.74. Found: C, 43.48; H, 4.31; N, 9.80; Ga, 12.21; I, 22.78.

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