

Figure 3.

Since the ultraviolet spectra serve as diagnostic tests of configuration in this series, it is easy to identify the stereoisomers of Ia-f (Fig. 3). The *trans* isomer is the higher melting (208–209°) and the *cis* isomer the lower melting (196–197°) form. This result is contrary to a previous assignment.² Accordingly, the configurations claimed² for the related acid and other derivatives must now be reversed.

The above conclusions are borne out by an inspection of the S–O stretching region in the infrared. The *cis* isomers of Ia–f all have a strong band at 1087–1094 cm.⁻¹ (KBr). The *trans* isomers on the other hand all have two regions of strong absorption, one at 1070–1079 cm.⁻¹ and the other at 1018–1044 cm.⁻¹. The low frequency band presumably corresponds to the a'-stretching mode.⁹

The isomerization¹⁰ of Ia on heating¹¹ is classically the first example of a thermal stereomutation in the sulfoxide series. Ib has also been thus isomerized¹² and this method has recently been extended to monosulfoxides.¹³ We find that the *trans* isomers of Ia–f all isomerize to the *cis* isomers at elevated temperatures (200–300°). The misassignment² of configuration was the result of the assumption, based on earlier erroneous conclusions,¹⁴ that the acid precursor of *trans*-Ia is the more stable form.

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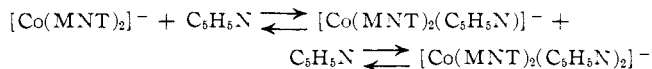
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Interconvertible Four-, Five-, and Six-Coordinate Cobalt Complexes¹

Sir:

Acetone solutions of salts of one or both of the interesting square-planar complexes, $\text{Co}(\text{MNT})_2^-$ and $\text{Co}(\text{TDT})_2^-$,² undergo color changes in the presence of the ligands pyridine, *o*-phen, triphenylarsine, triphenylphosphine, MNT^{2-} , and diars.³ In most cases crystalline complexes precipitate from the solutions on addition of ether. Elemental analyses reveal that the color changes follow from the formation of new complexes in which the coordination number of cobalt has increased to five or six. Six crystalline compounds giving good analyses have been isolated. They are the five-coordinate species $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Co}(\text{MNT})_2(\text{C}_6\text{H}_5\text{N})]$ and $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Co}(\text{MNT})_2(\text{P}(\text{C}_6\text{H}_5)_3)]$ and the six-coordinate species $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Co}(\text{MNT})_2(o\text{-phen})]$, $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Co}(\text{MNT})_2(\text{diars})]$,⁴ $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{Co}(\text{MNT})_3]$, and $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Co}(\text{TDT})_2(o\text{-phen})]$. In addition, the five-coordinate complex $[\text{Co}(\text{MNT})_2(\text{As}(\text{C}_6\text{H}_5)_3)]^-$ and the six-coordinate complexes $[\text{Co}(\text{MNT})_2(\text{C}_5\text{H}_5\text{N})_2]^-$ and $[\text{Co}(\text{TDT})_2(\text{diars})]^-$ were identified spectroscopically in solution. The solids are all diamagnetic and $[\text{Co}(\text{MNT})_2(\text{P}(\text{C}_6\text{H}_5)_3)]^-$ is diamagnetic in acetone solution. The final observation that, with the exception of $[\text{Co}(\text{MNT})_2(\text{C}_5\text{H}_5\text{N})]^-$, excesses of ligand do not modify the solution spectra leads to the conclusion that these stable adducts include the first examples of diamagnetic, truly five-coordinate cobalt in the formal oxidation state, "Co(III)."⁵

Table I contains a summary of the spectra of the new complexes in acetone. Spectra of the pyridine solutions show an absorption maximum developing at 705 μ m at low pyridine concentration which then decreases again at high pyridine concentration, leading finally to a weak band with a maximum at 700 μ m. This is interpreted by the reactions



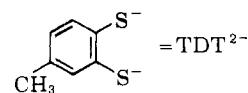
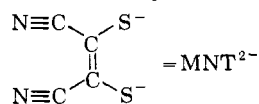
Fortunately, the successive stages of complex formation are fairly well separated. The successive formation constants for five- and six-coordination at 25° may be estimated as 3.5×10^3 and 5.5, respectively, and the spectrum of the five-coordinate species determined.

Formation constants for several of the other adducts were also determined spectrophotometrically. This could be done either by directly observing dissociation

(1) Acknowledgment is made to the National Science Foundation for support of this research. This research was also supported by Public Health Service Research Grant No. CA-07016-01 from the National Cancer Institute.

(2) (a) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963); (b) E. Billig, H. B. Gray, S. I. Shupack, J. H. Waters, and R. Williams, *Proc. Chem. Soc.*, 110 (1964).

(3) Abbreviations used: *o*-phenylene bis(dimethylarsine) = diars, 1,10-phenanthroline = *o*-phen



(4) Samples of this compound could not be obtained free of residual $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$.

(5) Five-coordinate, paramagnetic Co(III) complexes of the type $\text{Co}(\text{PR}_3)_2\text{X}_3$ have recently been prepared by K. A. Jensen, P. H. Nielsen, and C. T. Pedersen, *Acta Chem. Scand.*, **17**, 1115 (1963).

TABLE I
LOWER ENERGY SPECTRAL BANDS OF COBALT MNT COMPLEXES IN ACETONE^a

Complex	λ (log ϵ)			
[Co(MNT) ₂] ⁻	455 (3.7)	540 (3.5), sh	790 (3.6)	1345 (2.9)
[Co(MNT) ₂ (C ₆ H ₅ N)] ⁻	453 (3.4)		705 (3.2)	1100 (2.4)
[Co(MNT) ₂ P(C ₆ H ₅) ₃] ⁻	495 (3.5)		685 (2.7)	1225 (3.2)
[Co(MNT) ₂ As(C ₆ H ₅) ₃] ⁻	530 (3.0)		710 (2.3)	1330 (2.9)
[Co(MNT) ₃] ³⁻	460 (3.6)		665 (2.6)	
[Co(MNT) ₂ (C ₅ H ₅ N) ₂] ⁻	440 (3.4)		700 (2.6)	
[Co(MNT) ₂ (<i>o</i> -phen)] ⁻	428 (3.7)		655 (2.7)	
[Co(MNT) ₂ (diars)] ⁻	463 (3.7)		650 (3.2)	

^a Wave length of maxima and shoulders in m μ (log of molar extinction coefficient follows wave length in parentheses).

of the adduct or by running ligand displacement experiments. All of the compounds are reasonably labile so that equilibration is rapid. Only values for very stable *o*-phen and diars adducts of Co(MNT)₂⁻ were inaccessible. Apparently, TDT²⁻ increases the stability of the square-planar structure sufficiently to bring the formation constants for the corresponding *o*-phen and diars adducts of Co(TDT)₂⁻ down to fairly low values (note that only those two ligands yielded adducts with Co(TDT)₂⁻). Table II contains the values of formation constants for mono adducts with both five- and six-coordination. We can extract the order of ligand affinities for these complexes as diars > *o*-phen > P(C₆H₅)₃ > C₅H₅N > (C₆H₅)₃As.

TABLE II
FORMATION CONSTANTS OF "MONO ADDUCTS" IN ACETONE
AT 25°

Adduct	log K _f
[Co(MNT) ₂ As(C ₆ H ₅) ₃] ⁻	2.8
[Co(MNT) ₂ (C ₅ H ₅ N)] ⁻	3.5
[Co(MNT) ₂ P(C ₆ H ₅) ₃] ⁻	6.1
[Co(TDT) ₂ (<i>o</i> -phen)] ⁻	1.7
[Co(TDT) ₂ (diars)] ⁻	2.4

Although usual oxidation state formalism suggests that these complexes be designated "Co(III)," the chemical evidence presented here indicates the difficulties with this designation. Four characteristics of these complexes are not common among Co(III) complexes: (1) stable four-coordinate species, (2) stable five-coordinate species, (3) ready interconvertibility among four-, five-, and six-coordination, and (4) a ligand affinity order with P preferred to N as a donor (the Ahrlund, Chatt, and Davies "type B" or Pearson "soft acid" behavior).⁶ In fact, these properties, taken together, are consistent with the behavior of d⁸ systems and provide substantial support to our earlier electronic structural assignment^{2(a)} of d⁸ (metal) radical anion (ligand) for Co(TDT)₂⁻ and Co(MNT)₂⁻. An electronic interpretation of the analogy with d⁸ complexes follows by assuming that at least one *bonding* electron pair is *more nearly localized on the metal than on the ligands*.

The question of the structures of the five- and six-coordinate species is still open. The five-coordinate complexes probably have square-pyramidal geometry. Since the spectra of the six-coordinate species are not typical of octahedral Co(III), an interesting possibility is that the factors which stabilize the square-planar geometry in four-coordination may operate to produce

a trigonal prismatic, or at least a strongly trigonally distorted, six-coordinate structure.

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The Structure of Spinochrome M

Sir:

Research on spinochromes, the polyhydroxynaphthoquinone pigments from the spines and tests of sea urchins, has been characterized by an abundance of reported compounds and a paucity of substantiated facts.¹ This situation was dramatically illustrated in the recent communication by Gough and Sutherland,² who established the structure of spinochrome B and proved its identity with no fewer than six previously reported and supposedly different pigments.

Our own suspicion that the chemical literature offered a larger variety of spinochromes than did nature was strengthened when we examined six species of Hawaiian sea urchins in five genera and found that the same pigment occurred as the major pigment in the spines of *Echinometra oblonga* Blainville and *Colobocentrotus atratus* Linn., and as a minor constituent in the spines of *Tripneustes gratilla* Linn., *Echinothrix diadema* Linn., *E. calamaris* Pallis, and *Diadema paucispinum* Agassiz.

The spines were digested in concentrated hydrochloric acid and the pigments were extracted with ether, washed into aqueous sodium bicarbonate solution under nitrogen, and transferred into benzene after acidification with phosphoric acid. Separation of the pigments was achieved on a column of silica gel (load factor 1000:1), which had been pretreated with 0.5 N hydrochloric acid and dried at room temperature. Elution with benzene removed the major pigment, dark purple needles from methanol, m.p. 192–193°, or 183–184° as the methanol solvate; yield *ca.* 0.05% from *E. oblonga* or *C. atratus*. This pigment proved to be identical in all respects (melting point, ultraviolet spectra in three solvents, n.m.r., and thin-layer chromatogram) with an authentic sample of spinochrome M.³

We assigned to spinochrome M structure I (represented here is one of several quinoid tautomers)

(1) R. H. Thomson, "Naturally Occurring Quinones," Butterworths Scientific Publications, London, 1957, pp. 128–140.

(2) J. Gough and M. D. Sutherland, *Tetrahedron Letters*, 269 (1964).

(3) We are indebted to Drs. C. Kuroda and M. Okajima for a sample of spinochrome M.

(6) (a) S. Ahrlund, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 265 (1958); (b) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).