

or at least distorted from planar toward tetrahedral. The addition of the first mnt^{2-} group would then involve a change of stereochemistry from tetrahedral to planar (tetragonal). Swift reported²⁰ evidence that a stereochemical change from tetrahedral to octahedral can be slow relative to many ligand-substitution reactions for cobalt(II) and zinc(II). It is possible that the displacement of NTA from copper(II) by mnt^{2-} is slow compared to IDA and EDTA because the former displacement involves tetrahedral copper converting to planar whereas the latter involves planar or tetragonal copper without a change in stereochemistry. Even if the stereochemical change is not rate determining, we suggest that the difference in kinetics is due to the NTA complex being tetrahedral and hence possessing energy requirements for substitution qualitatively different from the planar complexes.

The electronic spectra of the copper(II) complexes reported herein have been published.²¹ The spectra of the EDTA and NTA complexes are not sufficiently different to allow any conclusions as to structure. None of the possible structures for $\text{Cu}(\text{NTA})^-$ possesses a center of inversion so intensity arguments are not really useful. Actually, destruction of a center of symmetry does not always lead to increased intensity.²²

We have found that the displacement of EDTA and NTA from cadmium(II) with mnt^{2-} under the conditions stated above is too rapid to observe on a stopped-flow device. The displacement of NTA from zinc(II) with mnt^{2-} is about ten times faster than from copper(II), but mnt^{2-} will not displace EDTA from zinc(II).

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Kinetics and Mechanisms of the Substitution Reactions of Five-Coordinate Cobalt Formally in Oxidation State III

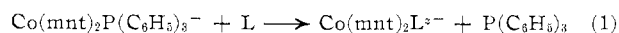
By DWIGHT A. SWEIGART AND DAVID G. DEWIT

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Maleonitriledithiolate (mnt) readily forms the complex $\text{Co}(\text{mnt})_2^-$ which has cobalt in a formal oxidation state of III. This complex forms a wide variety of

five- and six-coordinate adducts.^{1–3} The substitution reactions of these adducts are usually very rapid. It has been shown¹ that $\text{Co}(\text{mnt})_2^-$ displays many properties at variance with the usual behavior of cobalt(III) and the metal resembles a d^8 system more closely than a d^6 system. We have initiated an investigation of the kinetics of the unusual cobalt(III) and iron(III) maleonitriledithiolate systems.

Herein we report the kinetics of reaction 1, where $L = \text{en}$, bipy , phen , mnt^{2-} , $i\text{-mnt}^{2-}$, and triphenyl phosphite.



Experimental Section

Sodium maleonitriledithiolate (Na_2mnt) and its isomer sodium 1,1-dicyanoethylene-2,2-dithiolate ($\text{Na}_2(i\text{-mnt})$) were prepared and purified by published methods.^{4,5} The other nucleophiles were purchased. The reactions were studied in methanol, purified as previously described,⁶ at 25° on a commercially available⁷ stopped-flow device. The ionic strength was maintained at 0.1 M with sodium perchlorate. The $\text{Co}(\text{mnt})_2\text{P}(\text{C}_6\text{H}_5)_3^-$ complex was prepared *in situ* from triphenylphosphine and $[(\text{CH}_3)_4\text{N}]\text{Co}(\text{mnt})_2$ prepared by a published method.⁸ *Anal.* Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_3\text{S}_2\text{Co}$: C, 34.9; H, 2.9; N, 16.9. Found: C, 34.9; H, 2.8; N, 16.9. Spectra of reactants and products agreed with those previously reported.^{1–3} For the kinetic runs $\text{Co}(\text{mnt})_2^-$ was made 10^{-4} M and then triphenylphosphine was made either 10^{-4} M or 6×10^{-4} M , the latter representing a five-fold excess of triphenylphosphine over $\text{Co}(\text{mnt})_2\text{P}(\text{C}_6\text{H}_5)_3^-$.

Results and Discussion

Figure 1 shows the mechanism proposed to account for the observed kinetics with bidentate nucleophiles. We propose a similar mechanism for unidentate nucleophiles except that C represents the product so k_4 , k_5 , and k_7 do not operate. The results are presented in Figures 2–4. Table I lists the results for cases when

TABLE I
THE DEPENDENCE OF k_{obsd} ON NUCLEOPHILE CONCENTRATION
IN THE CASES EXHIBITING LINEAR BEHAVIOR

Nucleophile ^a	k_{obsd} , sec^{-1}	
	No excess $\text{P}(\text{C}_6\text{H}_5)_3$	Fivefold excess $\text{P}(\text{C}_6\text{H}_5)_3$ (5×10^{-4} M)
mnt^{2-}	$3.4 + 1900[\text{mnt}^{2-}]$	$0.32 + 507[\text{mnt}^{2-}]$
$i\text{-mnt}^{2-}$	$3.3 + 1140[i\text{-mnt}^{2-}]$	$0.21 + 262[i\text{-mnt}^{2-}]$
phen	$0.24 + 425[\text{phen}]$	$79[\text{phen}]$

^a Nucleophile concentration was in the range $(1-7) \times 10^{-3}$ M .

linear k_{obsd} vs. nucleophile concentration plots were obtained. Assuming the steady-state approximation for B and C one obtains, for excess L-L

$$k_{\text{obsd}} = \frac{k_1 k_3 k_5 [\text{L-L}] + k_3 k_6 K [\text{L-L}] (k_2 [\text{P}] + k_3 [\text{L-L}])}{(1 + K [\text{L-L}]) (k_2 [\text{P}] (k_4 + k_5 + k_7 [\text{P}]) + k_3 [\text{L-L}] (k_5 + k_7 [\text{P}]))} \quad (2)$$

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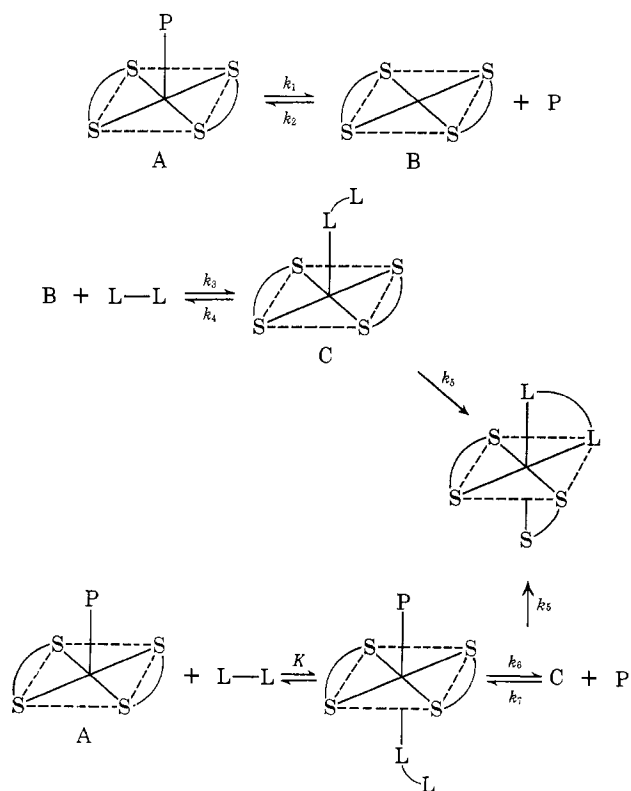


Figure 1.—Proposed mechanism for substitution with bidentate nucleophiles: L-L, nucleophile; S-S, mnt; P, triphenylphosphine. Charges are omitted.

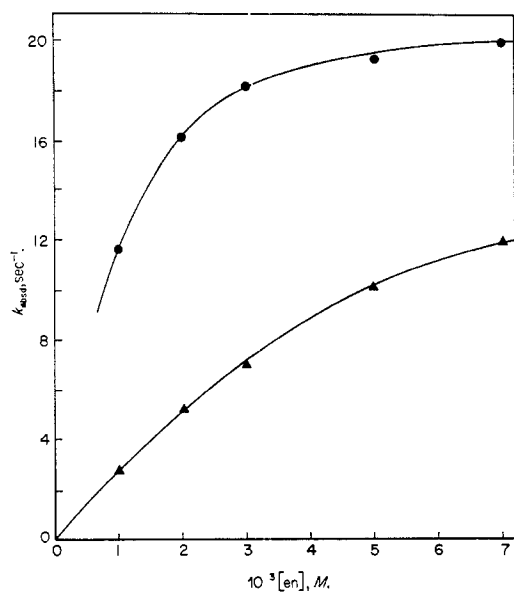


Figure 2.—The dependence of k_{obsd} on nucleophile concentration for L-L = ethylenediamine: ●, no excess triphenylphosphine; ▲, fivefold excess triphenylphosphine ($5 \times 10^{-4} M$).

For unidentate nucleophiles eq 3 obtains. Equation 2

$$k_{\text{obsd}} = \frac{k_1 k_3 [\text{L}]}{(1 + K[\text{L}])(k_2[\text{P}] + k_3[\text{L}])} + \frac{k_6 K[\text{L}]}{1 + K[\text{L}]} \quad (3)$$

predicts that a limiting k_{obsd} equal to $k_5 k_6 / (k_5 + k_7[\text{P}])$ should be reached as [L-L] becomes large. This is seen for en and bipy (Figures 2 and 3). Also predicted by eq 2 is that all k_{obsd} values are lowered when excess leaving group (P) is present. Figures 2 and 3 show

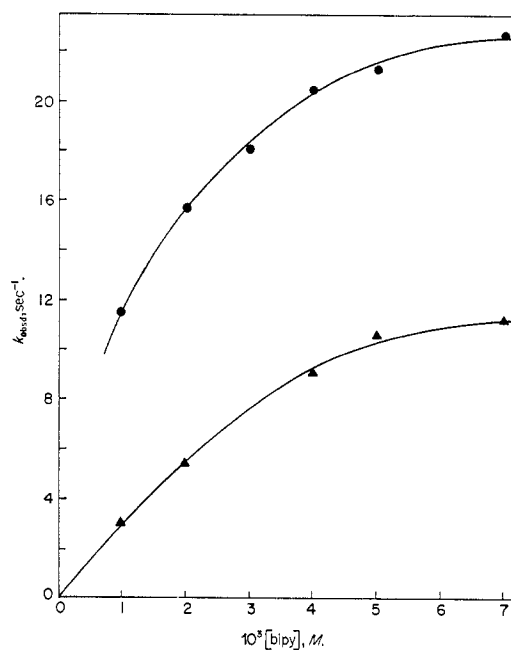


Figure 3.—The dependence of k_{obsd} on nucleophile concentration for L-L = bipyridine: ●, no excess triphenylphosphine; ▲, fivefold excess triphenylphosphine ($5 \times 10^{-4} M$).

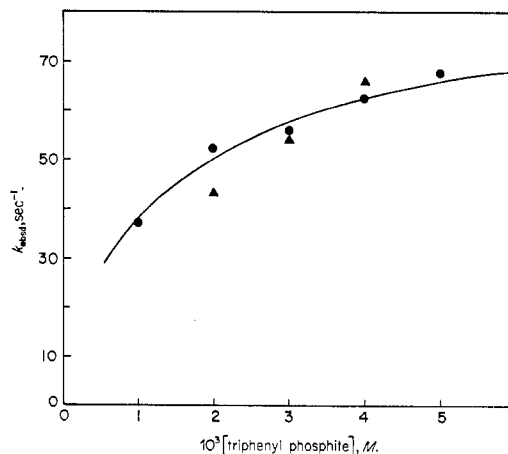


Figure 4.—Dependence of k_{obsd} on nucleophile concentration for L = triphenyl phosphite: ●, no excess triphenylphosphine; ▲, fivefold excess triphenylphosphine ($5 \times 10^{-4} M$).

that this indeed occurs. The intercepts should be zero when excess P is present and equal to k_1 when no P is present. Of course some P is generated during the course of the reaction so that k_1 is an upper limit to the intercept. The figures and Table I show that the intercepts drop close or equal to zero when excess P is present. Actually eq 2 predicts that when a large relative change in [P] occurs, as when no excess P is added, good pseudo-first-order kinetics may not be seen. We found slight curvature in the kinetic plots when excess P was zero. This occurred because P is generated during the course of the reaction. The curvature was small, however, and reliable k_{obsd} values were obtained. With P added in excess rigorously first-order plots were obtained. Figure 4 shows that with triphenyl phosphite as the nucleophile a limiting rate seems to be reached, although the k_{obsd} values are large, being near our limit of measurement. Equation

3 yields a limiting rate constant equal to k_6 and predicts that excess leaving group (P) will have no effect on this limit. This is indeed found to be the case. With a large excess of triphenyl phosphite it is likely that $k_3[L] \gg k_2[P]$ and then eq 3 demands that excess P have no effect on the plot of k_{obsd} vs. nucleophile concentration. Figure 4 shows that this is the case within experimental error, except possibly at the lowest nucleophile concentration where the inequality is least likely to be valid. This behavior is in sharp contrast to that of the bidentate nucleophiles discussed above.

Table I shows that 1,10-phenanthroline (phen) is much less reactive than the other nucleophiles. This we attribute to the well-known inflexibility of phen relative to en and bipy.^{9,10} The intercept is well below that of mnt^{2-} and $i\text{-mnt}^{2-}$ and we attribute this to the fact that the triphenylphosphine can compete more favorably in this case.

The mechanism shown in Figure 1 involves an associative and a dissociative pathway. We have been unable to formulate any other reasonable mechanism that is consistent with the data. The nonzero intercepts for the ligands in Table I are the principal results suggesting a partial dissociative pathway. Our conclusion is that the substitution reactions proceed *via* two pathways, both of which contribute significantly to the overall reaction. As the nucleophile concentration increases, the associative pathway becomes more and more predominant. At low nucleophile concentrations the dissociative path predominates (Table I).

An attempt was made to study reaction 1 with iron as the metal. Unlike the cobalt system, it was found that a large excess of $\text{P}(\text{C}_6\text{H}_5)_3$ was needed to form $\text{Fe}(\text{mnt})_2\text{P}(\text{C}_6\text{H}_5)_3^-$ to any detectable extent, rendering a kinetic investigation infeasible.

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Absorption Spectrum of Vanadium(II) Chloride from 5000 to 30,000 Cm^{-1}

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In the preparation of VCl_2 for heat capacity measurements we obtained several pale green single crystal plates, about 0.2 mm thick and up to 1 cm in the

two other dimensions, which were of suitable quality for spectroscopic measurements. Since relatively few measurements have been reported of the crystal spectra of V^{2+} ($3d^3$) compounds, we have measured the absorption spectrum of VCl_2 in the range 5000–30,000 cm^{-1} and report the results here.

VCl_2 crystallizes in the CdI_2 -type structure^{1,2} and the crystals cleave readily along planes normal to the hexagonal c axis. The small dimension of the crystallites we obtained was parallel to this axis and only the axial spectrum, unpolarized light propagated parallel to the hexagonal axis, was measured.

Experimental Section

VCl_2 was prepared by treating vanadium metal, ground to 20 mesh, with dry HCl gas at 950°. Pale green crystal plates collected in the cooler portion of the quartz reaction tube. A sample of the VCl_2 was analyzed for vanadium by titration with standard 0.1 N KMnO_4 solution and for chlorine gravimetrically by precipitation of AgCl . *Anal.* Calcd for VCl_2 : V, 41.81; Cl, 58.19. Found: V, 41.69; Cl, 57.95. The only impurities seen in a spectrochemical analysis were, in weight per cent: Mg, 0.001; Si, 0.01; Fe, 0.05; Cu, 0.001.

The spectra were measured with a Cary Model 14 spectrophotometer. The crystal of VCl_2 was mounted on a copper plate with an accurately machined aperture and assembled in the lower section of a cryostat which also carried an empty matched aperture. The lower section of the cryostat could be rotated to place either the blank aperture or the crystal in the beam of the spectrophotometer, and the difference between the measured absorbance of the crystal and the blank was determined. The temperature of the copper plate on which the VCl_2 crystal was mounted was measured with a copper-constantan thermocouple. Spectra were measured at room temperature and with liquid helium in the cryostat reservoir in thermal contact with the sample holder. The principal uncertainty in the molar extinction coefficients arises from uncertainties in the thickness of the crystals. The thickness of one sample of VCl_2 which was fairly uniform was determined by measurement of weight and area (0.88 cm^2) and also with a micrometer caliper. The average thickness was 0.08 ± 0.02 mm. Thicknesses of other samples on which spectra were measured were determined by comparison of the room-temperature absorbance of the 8.98×10^3 and 13.92×10^3 cm^{-1} peaks with those measured for the sample whose thickness was most accurately measured. Small corrections for surface reflection and scattering were made by drawing a base line through the measured absorbances at 17,000 and 5800 Å in the liquid helium experiments.

Results

The molar extinction coefficients of VCl_2 at 298 and 22°K are plotted vs. wave number in Figures 1 and 2. The errors in the extinction coefficients are $\pm 25\%$ because of uncertainty in thickness of the sample, but the relative error of various parts of the spectrum below 29×10^3 cm^{-1} is less than 10%. In Table I are listed the wave numbers of the principal peaks observed in the spectra at 22 and 298°K. The two strong near-infrared bands and the very narrow absorption at 15.940×10^3 cm^{-1} seen in the 22°K spectrum are well separated from other features. These curves are Gaussian in shape, and their width at half-height, $\Delta\nu$, and the oscillator strength, f (uncorrected for refractive index), are listed in Table I. Above 19×10^3 cm^{-1} the spectrum is not resolvable into well-

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