CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Transition Metal Complexes of the N-Cyanocarbimate Ion, $[S_2C_2N_2]^{2-}$

BY F. A. COTTON AND J. A. McCLEVERTY

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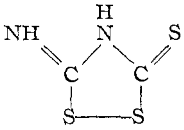
The chemistry of the so-called "dithiocyanate ion," $S_2C_2N_2^{2-}$, obtained by treatment of xanthane hydride with base, has been studied, principally in regard to the formation of complexes in which it functions as a bidentate chelating ligand. It is concluded that this ion is identical with the N-cyanodithiocarbimate ion, $S_2C{=}N{-}CN^{2-}$, of Fackler and Coucouvanis, and that it does indeed have the structure implied by this name. The preparation and properties of $M(S_2C_2N_2)_2^{n-}$ compounds (n = 2 for M = Ni, Pd, Cu, Zn; n = 1 for M = Au; n = 3 for M = Tl) and $[(C_6H_5)_3P]_2M(S_2C_2N_2)$ compounds (M = Ni, Pd, Pt) are described.

Introduction

The compound xanthane hydride was discovered nearly a century ago.[1] On the basis of chemical evidence Hantzsch and Wolvekamp[2] proposed structure I for it, but an X-ray crystallographic study[3] has shown that, in the crystal at least, the correct tautomeric form is II. Structure II has also received support from infrared studies[4a,c] and it has also been shown[4b,c] by infrared study that a compound isomeric with this probably has structure III.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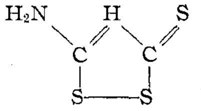
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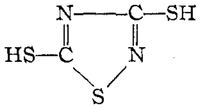
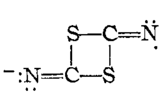
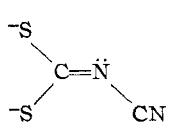

III

One of the earliest reactions of xanthane hydride to be discovered[5] is that with potassium hydroxide, leading to the formation of the potassium salt of what has been called the "dithiocyanate ion," $C_2S_2N_2^{2-}$, for which a cyclic structure, IV, was originally proposed.[1] On chemical evidence, Hantzsch and Wolvekamp[2] proposed instead the carbamate-like structure, V.


IV


V

Their reasoning, though plausible, is far from unequivocal, nor did it appear possible, when the studies described in this report were commenced, several years ago, to deduce a structure definitively from chemical evidence alone. Moreover, at the time we became interested in this problem, no work beyond that outlined above was found in the literature, except for Fleischer's report[5] that potassium, copper(II), lead(II), silver(I), and ammonium "salts," as well as the acid itself, $H_2C_2S_2N_2$, and its diethyl ester, could be isolated. This work shed no further light on the structural question, however.

This novel and not well-characterized system seemed to merit investigation from two points of view. First, we wished to determine if the reported existence of "salts" with transition metal ions implied that the $C_2S_2N_2^{2-}$ ion had the ability to function as a ligand and, if so, to isolate and characterize representative complexes. Second, it was hoped that one of the complexes so obtained could be used for a single-crystal X-ray study which would unequivocally answer the structural question.

After this study was essentially complete, we learned of the work of Fackler and Coucouvanis,[6] who were led to prepare and characterize some of the same complexes (with different accompanying cations) for rather different reasons. These authors began by assuming that a general class of 1,1-dithio anionic ligands, $S_2C{=}X^{2-}$, should exist, one of them having X equal to ${=}N{-}CN$. They prepared this anion by a rational route (from $NCN^{2-} + CS_2$) which would be expected to lead to structure V, though, again, the possibility of rearrangement could not be entirely discounted.

However, their complexes, as the tetra-*n*-propylammonium salts of $M(C_2S_2N_2)_2^{2-}$ (M = Ni, Pd, Pt), appear to be identical with ours. Moreover, it has been shown by a single-crystal X-ray study[7] of $[(C_6H_5)_4As]_2[Ni(S_2C_2N_2)_2]$, that the complex anion is a planar, four-coordinate complex of nickel, in which the ligands do indeed have structure V. Thus the reasoning and structural conclusions of Fackler and Coucouvanis are substantiated and the nature of the "dithiocyanate ion" is revealed. In view of its true structure, V, the best name for it would appear to be that suggested[6b] by Fackler and Coucouvanis, *viz.*, N-cyanodithiocarbimate.

Experimental Section

Preparation of Compounds.—All chemicals were of reagent grade and were used without further purification. Melting points are uncorrected.

Xanthane Hydride, $H_2S_3C_2N_2$.—This was prepared by a method similar in general to that outlined in the older literature,[1] but the details have not been explicitly stated. Ammonium thiocyanate (453 g) was dissolved in 2 l. of water, and 500 ml of concentrated HCl was added. A white precipitate formed immediately, but

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[1] W. v. Schneider and E. Erlenmeyer, *Ber.*, **3**, 339 (1870).
[2] A. Hantzsch and M. Wolvekamp, *Ann.*, **331**, 265 (1904).
[3] A. Hordvik, *Acta Chem. Scand.*, **17**, 2575 (1963).
[4] (a) H. J. Emeléus, A. Haas, and N. Sheppard, *J. Chem. Soc.*, 3165 (1963); (b) *ibid.*, 3168 (1963); (c) these authors call xanthane hydride "isoperthiocyanic acid" and its isomer "perthiocyanic acid."
[5] A. Fleischer, *Ann.*, **179**, 204 (1875).
[6] (a) J. P. Fackler, Jr., and D. Coucouvanis, *Chem. Commun.*, 556 (1965); (b) *J. Am. Chem. Soc.*, **88**, 3913 (1966).
[7] F. A. Cotton and C. B. Harris, to be published.

after 10 min the reaction mixture had become tinged with yellow. The mixture was left to stand at 20–25° for 16 hr, and the yellow-orange solid was then separated by filtration. The solid was washed with 150-ml portions of water, methanol, and ethyl ether, in that order, and then allowed to dry in the air; yield, 69 g, 23% based on NH_4NCS. The compound was soluble in $CHCl_3$ and CH_2Cl_2, moderately soluble in benzene, acetone, and ethanol, but insoluble in ether and aliphatic hydrocarbons.

Anal. Calcd for $C_2H_2N_2S_3$: C, 16.00; H, 1.33; N, 18.67; S, 64.00. Found: C, 16.4; H, 1.6; N, 18.5; S, 63.8.

$\mathbf{K_2S_2C_2N_2}$.—This was prepared by the method of Hantzsch and Wolvekamp[2] with only the minor modification of extracting the filtrate in 5-ml portions, each with *ca.* 300 ml of absolute ethanol, instead of extracting the entire quantity at once. The yield was 5.5 g (17%) from 25 g of xanthane hydride.

$\mathbf{[(CH_3)_4N]_4[Ni(S_2C_2N_2)_2]}$.—To a solution of $Ni(ClO_4)_2 \cdot 4H_2O$ (3.3 g) in water (20 ml) was added a solution of $K_2S_2C_2N_2$ (3.8 g) in water (10 ml). Immediately the mixture changed from a pale green to an intense emerald-green. After standing at 0° for 30 min, the solution was filtered to remove $KClO_4$ and $(CH_3)_4NBr$ (3.2 g) in water (30 ml) was added. Slowly, olive-green platelets began to form, and, after standing at 0° for 4 hr, 3.6 g of the complex, mp 230–232° dec, was collected by filtration, washed rapidly with methanol and anhydrous ether, and air dried; yield, 82%, based in $Ni(ClO_4)_2 \cdot 4H_2O$.

Anal. Calcd for $C_{12}H_{24}N_6S_4Ni$: C, 32.8; H, 5.5; N, 19.1; S, 29.2. Found: C, 32.9; H, 5.5; N, 19.2; S, 29.4.

The complex is very soluble in dimethyl sulfoxide, dimethylformamide, and nitromethane; large crystals can be obtained from the latter solution if it is allowed to evaporate slowly at room temperature. It is sparingly soluble in acetone and ethanol and insoluble in other common organic solvents.

$\mathbf{Cs_2Ni(S_2C_2N_2)_2}$.—To a solution of $NiCl_2 \cdot 6H_2O$ (1.2 g) in water (40 ml) was added a solution of $K_2S_2C_2N_2$ (2.0 g) in water (20 ml) and the deep green solution was filtered. To this solution was added CsCl (1.7 g) and the mixture was evaporated to 30 ml on a steam bath. The solution was then cooled at 0° overnight and dark green crystals formed. These were filtered, washed rapidly with water, ethanol, and anhydrous ether, in that order, and air dried; yield, 1.8 g, 66% based on $NiCl_2 \cdot 6H_2O$. The compound is sparingly soluble in water, acetone, and alcohols.

Anal. Calcd for $C_4N_4S_4Cs_2Ni$: C, 8.6; N, 10.1; S, 23.0. Found: C, 8.6; N, 10.1; S, 23.0.

$\mathbf{[(CH_3)_4N]_2[Pd(S_2C_2N_2)_2]}$.—$PdCl_2$ (1.8 g) was suspended in an aqueous solution of $K_2S_2C_2N_2$ (3.9 g in 100 ml of H_2O) and shaken for 4 hr at room temperature. During this time the solution changed from brown-yellow to cherry-red. The solution was filtered and $(CH_3)_4NBr$ (3.1 g) was added to the filtrate. Immediately, orange-yellow crystals began to form, and, after 30 min, they were collected by filtration, washed with methanol and then anhydrous ether, and recrystallized from hot nitromethane; mp 257–258° dec; yield, 2.7 g, 68% based on $PdCl_2$.

Anal. Calcd for $C_{12}H_{24}N_6S_4Pd$: C, 29.6; H, 4.9; N, 17.3; S, 26.3. Found: C, 29.7; H, 4.9; N, 17.2; S, 26.4.

The complex has solubility properties similar to those of its nickel analog. Crystals suitable for single-crystal X-ray studies were readily obtained from hot nitromethane solutions.

$\mathbf{Cs_2Cu(S_2C_2N_2)_2}$.—$Cs_2CuCl_4$ (1.5 g) in water (100 ml) was treated slowly and with shaking with $K_2S_2C_2N_2$ (1.3 g) in water (50 ml). The red solution was filtered and cooled, and an orange-red solid began to settle out slowly. After 2 hr the solid was collected by filtration, washed with methanol and anhydrous ether, and dried under vacuum at 100°; yield, 0.6 g, 43% based on Cs_2CuCl_4. The compound is insoluble in common solvents and is readily decomposed by acids.

Anal. Calcd for $C_4N_4S_4Cs_2Cu$: C, 8.5; N, 10.0; S, 22.7. Found: C, 8.5; N, 10.0; S, 22.8.

$\mathbf{[(CH_3)_4N][Au(S_2C_2N_2)_2]}$.—$HAuCl_4 \cdot 3H_2O$ (3.9 g) was dissolved in water (100 ml), and $K_2S_2C_2N_2$ (3.9 g) in water (20 ml) was added. The cloudy yellow mixture was filtered, and to the yellow filtrate was added $(CH_3)_4NBr$ (1.6 g) in water (30 ml). The yellow solid which precipitated immediately was filtered off, washed rapidly with cold ethanol and anhydrous ether, and recrystallized from hot methanol; mp 172–174° dec; yield, 3.3 g, 66% based on $HAuCl_4 \cdot 3H_2O$.

Anal. Calcd for $C_8H_{12}N_5S_4Au$: C, 19.1; H, 2.4; N, 13.9; S, 25.5. Found: C, 19.4; H, 2.4; N, 13.4; S, 25.3.

The compound is soluble in acetone and alcohols but sparingly soluble in methylene dichloride and insoluble in ethers and hydrocarbons.

$\mathbf{[(C_6H_5)_4As]_2[Zn(S_2C_2N_2)_2]}$.—To a solution of $[(C_6H_5)_4As]_2[ZnCl_4]$ (1.6 g) in acetone (100 ml) was added $K_2S_2C_2N_2$ (0.7 g) dissolved in water (30 ml) and acetone (10 ml). A faint, white precipitate formed initially but redissolved. After addition of the $K_2S_2C_2N_2$ solution, the mixture was filtered and enough water was added to the filtrate to initiate precipitation, and the solution was left to stand at 0° for 24 hr. White needles formed in the solution and these were collected by filtration, washed with ice-cold methanol and anhydrous ether, and air dried, mp 242–244° dec; yield, 1.1 g, 62% based on $[(C_6H_5)_4As]_2[ZnCl_4]$.

Anal. Calcd for $C_{52}H_{40}N_4S_4As_2Zn$: C, 58.7; H, 3.8; N, 5.2; S, 12.0; As, 14.1 Found: C, 58.5; H, 3.9; N, 5.2; S, 12.0; As, 14.0.

The complex is soluble in acetone and alcohols but insoluble in water, ether, and hydrocarbons.

$\mathbf{[(C_6H_5)_4P]_3[Tl(S_2C_2N_2)_3]}$.—To a solution of $[(CH_3)_4N][TlBr_4]$[8] (1.2 g) in acetone (50 ml) was added $K_2S_2C_2N_2$ (1.2 g) in a mixture of H_2O (30 ml) and acetone (10 ml). The solution turned yellow immediately. To this solution was added $(C_6H_5)_4PCl$ (2.3 g) in H_2O (25 ml) and acetone (10 ml), and immediately a cloudy yellow precipitate formed. On standing overnight, a yellow oil formed; the mother liquor was decanted and washed rapidly with cold acetone. The residue was then dissolved in the minimum of methylene chloride, and the deep yellow solution was filtered. The filtrate was added dropwise and with vigorous stirring to a large excess of *n*-pentane, and a flocculent, pale yellow precipitate was obtained. This was filtered out, washed with *n*-pentane, and air dried; mp 299–301° dec; yield, 2.4 g, 76% based on $[(CH_3)_4N][TlBr_4]$.

Anal. Calcd for $C_{78}H_{60}N_6S_6P_3Tl$: C, 60.0; H, 3.8; N, 5.4; S, 12.2. Found: C, 59.7; H, 3.9; N, 5.2; S, 12.0.

The complex is soluble in acetone and alcohol, sparingly soluble in methylene chloride, and insoluble in ether and hydrocarbons.

$\mathbf{[(C_6H_5)_4As]_2[S_2C_2N_2]}$.—To a solution of $K_2S_2C_2N_2$ (1.9 g) in water (20 ml) was added a solution of $(C_6H_5)_4AsCl$ (4.2 g) in water (50 ml). The pale yellow precipitate was filtered off and washed rapidly with methanol. The pale yellow solid was dissolved in a mixture of acetone and ether (2:1), and the solution was allowed to evaporate slowly through a polyethylene membrane at room temperature. Large, colorless crystals, mp 270–272°, were formed; yield, 3 g, 34% based on $K_2S_2C_2N_2$.

Anal. Calcd for $C_{50}H_{40}S_2N_2As_2$: C, 68.0; H, 4.5; N, 3.2; S, 7.3; As, 17.0. Found: C, 67.6; H, 4.7; N, 3.1; S, 7.3; As, 16.7.

The compound is moderately soluble in acetone and slightly soluble in ether, methylene chloride, and methanol, but insoluble in water and other common organic solvents.

$\mathbf{\{[(C_6H_5)_3P]_2Ni(S_2C_2N_2)\}}$.—A suspension of $[(C_6H_5)_3P]_2NiCl_2$ (3.9 g) and $K_2S_2C_2N_2$ (2.0 g) in water (20 ml) and ethanol (50 ml) was shaken for 24 hr during which time the color of the mixture changed from dark green to salmon-pink. The mixture was filtered and the pink residue was washed thoroughly with water, methanol, and finally anhydrous ether; mp 250–252° dec; yield, 5.1 g, 72% based on $[(C_6H_5)_3P]_2NiCl_2$.

Anal. Calcd for $C_{38}H_{30}N_2S_2P_2Ni$: C, 65.2; H, 4.3; N, 6.0. Found: C, 65.1; H, 4.5; N, 4.4.

The compound is sparingly soluble in acetone and methylene chloride but insoluble in other common organic solvents.

$\mathbf{\{[(C_6H_5)_3P]_2Pd(S_2C_2N_2)\}}$.—$[(C_6H_5)_3P]_2PdCl_2$ (1.0 g) was dissolved in acetone (100 ml) and shaken with $K_2S_2C_2N_2$ (0.3 g) for

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(8) F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965).

24 hr. The mixture was then filtered, and the pale yellow residue was washed with water, methanol, and anhydrous ether. The solid was then dissolved in methylene chloride, and the solution was filtered and evaporated, affording 0.7 g of the complex, mp 275–277° dec; yield, 65% based on $[(C_6H_5)_3P]_2PdCl_2$.

Anal. Calcd for $C_{38}H_{30}N_2S_2P_2Pd$: C, 61.1; H, 4.0; N, 3.8; S, 8.6. Found: C, 60.9; H, 4.1; N, 3.9; S, 8.5.

The compound is soluble in acetone, methylene chloride, and chloroform, slightly soluble in alcohols, but insoluble in ether and hydrocarbons.

$\{[(C_6H_5)_3P]_2PtS_2C_2N_2\}$.—$[(C_6H_5)_3P]_2PtCl_2$ (1.1 g) was shaken with $K_2S_2C_2N_2$ (0.3 g) in chloroform (150 ml) for 24 hr. The mixture was filtered leaving a white residue. This was washed with water, methanol, and anhydrous ether and recrystallized from methylene chloride; mp 330–331° dec; yield, 0.75 g, 63% based on $[(C_6H_5)_3P]_2PtCl_2$. The compound has solubility properties similar to those of its palladium analog.

Anal. Calcd for $C_{38}H_{30}N_2S_2P_2Pt$: C, 54.6; H, 3.6; N, 3.4; S, 7.7. Found: C, 54.8; H, 3.4; N, 3.4; S, 7.7.

Spectra.—Infrared spectra were recorded using a Perkin-Elmer 337 infrared spectrometer and employing hydrocarbon and halocarbon oils as mull media. Some representative data are given in Table I. Visible spectra were measured using a Cary Model 14 recording spectrophotometer for solutions and a Beckman DU for the reflectance spectrum. Data are presented in Table II.

TABLE I

INFRARED SPECTRA OF SOME N-CYANODITHIOCARBIMATE COMPLEXES[a,b]

$L_2Ni(S_2C_2N_2)$	$L_2Pd(S_2C_2N_2)$	$L_2Pt(S_2C_2N_2)$	L_2PdCl_2
2180 vs	2175 vs	2177 vs	
1490 s	1470 s	1480 s	1490 s
1440 s	1430 s	1435 vw	1450 s
1310 vw	1310 vw	1258 vw	1318 w
1184 w	1183 w	1182 w	1187 w
1159 w	1159 w	1157 w	1160 w
1099 sh	1100 sh	1100 sh	1120 w
1090 m	1092 m	1092 m	1100 s
1070 sh	1070 vw	1068 vw	1095 sh
	1050 vw	1045 vw	
1028 vw	1028 vw	1027 vw	1029 vw
1010 w	1010 w	1008 w	1000 w
1000 w	1000 w	997 w	
	970 w	963 sh	972 w
959 s	958 s	955 m	
915 vw	914 vw	914 vw	918 vw
890 vw	890 vw	888 vw	890 vw
844 w	848 w	847 w	840 vw
755 m	758 m	757 w	754 m
735 s	745 sh	744 m	749 s
720 sh	740 m	737 s	724 w
704 sh	703 s	705 s	710 w
690 vs	692 vs	690 s	695 s

[a] Absorption peaks in cm^{-1}; s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] L represents triphenylphosphine.

Electrolytic Conductances.—These were measured with a commercially available Wheatstone bridge circuit and are recorded in Table III.

Results

Most of the complexes reported here are of two general types: $[M(S_2C_2N_2)_2]^{n-}$ ($M = Ni^{II}, Pd^{II}, Cu^{II}, Au^{III}, Zn^{II}$) and $((C_6H_5)_3P)_2ML$ ($M = Ni^{II}, Pd^{II}, Pt^{II}$). In addition, $[Tl(S_2C_2N_2)_3]^{3-}$ has been characterized. Comparing these stoichiometries with the known preference of all of the metal ions (except Tl(III)) for a coordination number of four, it would appear rather certain that $S_2C_2N_2^{2-}$ functions as a chelating bidentate ligand.

TABLE II

VISIBLE ABSORPTION MAXIMA

Compound	Solvent	ν_{max}, cm^{-1}	ϵ_{max}, M^{-1}
$[(CH_3)_4N]_2[Ni(S_2C_2N_2)_2]$	CH_3NO_2	16,000	74
		18,000–20,000 sh	~150
		~22,200 sh	~1.5 × 10^3
		24,100	10^4
$[(C_6H_5)_4P]_2[Ni(S_2C_2N_2)_2]$	Nujol mull	16,100	...[a]
		24,100	...[a]
$[(CH_3)_4N]_2[Pd(S_2C_2N_2)_2]$	CH_3NO	~22,800	240
		25,600	390
		28,300	5.9 × 10^3
$[(CH_3)_4N][Au(S_2C_2N_2)_2]$	CH_3NO	22,500	270
		27,000	3.7 × 10^3

[a] Intensities not measurable.

TABLE III

ELECTROLYTIC CONDUCTANCES IN NITROMETHANE[a]

Compound	Molar conductance, ohm^{-1} $mole^{-1}$	Temp, °C
$[(CH_3)_4N]_2[Ni(C_2N_2S_2)_2]$	210	25
$[(CH_3)_4N]_2[Pd(C_2N_2S_2)_2]$	204	25
$[(CH_3)_4N][Au(C_2N_2S_2)_2]$	75	25
$[(C_6H_5)_3As]_2(C_2N_2S_2)$	202	25
A^+B^-, typical[a,b–d]	80–100	20–25
$A^{2+}B_2^-$ or $A_2^+B^{2-}$, typical[c]	150–200	20
$A^{3+}B_3^-$, typical[c]	260	20

[a] All refer to *ca.* 10^{-3} *M* solutions. [b] C. M. Harris and T. N. Lockyer, *J. Chem. Soc.*, 3083 (1959). [c] N. S. Gill and R. S. Nyholm, *ibid.*, 3997 (1959). [d] J. E. Fergusson and R. S. Nyholm, International Conference on Coordination Chemistry, London, 1959, No. 62.

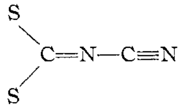
The colors of our $Ni(S_2C_2N_2)_2^{2-}$ and $Pd(S_2C_2N_2)_2^{2-}$ compounds are green and orange-yellow, in accord with the observations of Fackler and Concouvanis[6b] on their different compounds containing these same complex anions. More quantitatively, the visible spectra of their and our compounds containing the $Ni(S_2C_2N_2)_2^{2-}$ and $Pd(S_2C_2N_2)_2^{2-}$ ions are essentially identical, due allowance being made for the use of different solvents in the two studies. Moreover, despite the fact that minor features such as shoulders do not show up in the spectrum of the solid $[(C_6H_5)_4P]_2[Ni(S_2C_2N_2)_2]$, its major features are virtually identical with those found for the $[(n\text{-}C_3H_7)_4N]_2[Ni(S_2C_2N_2)_2]$ and $[(CH_3)_4N]_2[Ni(S_2C_2N_2)]$ compounds in solution, indicating that the structure of the $Ni(S_2C_2N_2)_2^{2-}$ complex is phase invariant.

The conductance data in Table III indicate that the stoichiometries and ionic formulations of the compounds are correct as given. These results compare very satisfactorily with those of Fackler and Coucouvanis,[6b] making allowance for the fact that their much larger cation and slightly lower temperature should lead to somewhat lower conductances.

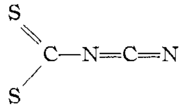
Aside from the compounds which are analogous to those of Fackler and Coucouvanis, we have also isolated the Ni, Pd, and Pt complexes of the type $[(C_6H_5)_3P]_2M(S_2C_2N_2)$, which are presumably the expected *cis*, planar, four-coordinate complexes.

The infrared spectra provide no useful information beyond that given by the C≡N stretching frequency. Fackler and Coucouvanis[6] have already given representative data for the $M(S_2C_2N_2)_2^{2-}$ compounds. Table I gives the bands observed in the $[(C_6H_5)_3P]_2M(S_2C_2N_2)$ compounds, together with the spectrum of $[(C_6H_5)_3P]_2PdCl_2$ for comparison. It is evident that no reliable indication of the positions of C=N or C—N stretching bands or of any other fundamentals of the N-cyanocarbimate ion is obtained. In these molecules as in the various $M(S_2C_2N_2)_2^{n-}$ ions[9] the C≡N band is in the range 2160–2180 cm^{-1}.

It is interesting to note that the "C≡N" band is very close to this range, *viz.*, 2150 cm^{-1}, in $K_2S_2C_2N_2$, whereas in $[(C_6H_5)_4As]_2S_2C_2N_2$, a new compound, it is around 100 cm^{-1} lower, namely, at 2050 cm^{-1}. Presumably the anion may be considered to be a resonance hybrid of Va and Vb, with Va preponderant. We then assume that potassium ions lie close to the sulfur atoms in $K_2S_2C_2N_2$ and, like the metal ions in the true complexes, tend to minimize the contribution of Vb, whereas in the $(C_6H_5)_4As^+$ salt, where no close approach of the sulfur atoms to a positive ion is possible, Vb makes a more significant contribution to the electron distribution, thus lowering the "C≡N" stretching frequency.



Va



Vb

Discussion

Though none of our compounds is identical with those of Fackler and Coucouvanis, the general similarity in properties at every point where comparison is possible leaves no reasonable doubt that the "dithiocyanate ion" prepared from xanthane hydride and the N-cyanodithiocarbimate ion of Fackler and Coucouvanis are one and the same. The X-ray study[7] of $[(C_6H_5)_4As]_2[Ni(S_2C_2N_2)_2]$ then shows that the structure of the $S_2C_2N_2^{2-}$ ion is V, that is, precisely the structure implied by the name N-cyanodithiocarbimate.

The study reported here is somewhat incomplete with respect to detailed study and interpretation of electronic spectra and other physical properties. However, because it is now clear that these compounds form a part of the general class of $S_2C{=}X^{2-}$ derivatives being broadly studied by Fackler and his co-workers, our own investigations, except for the aforementioned X-ray study, have been terminated at this stage.

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[9] In addition to those frequencies reported previously,[6b] we find the following (where L represents $S_2C_2N_2^{2-}$): AuL_2^-, 2180 cm^{-1}; ZnL_2^{2-}, 2166 cm^{-1}; CuL_2^{2-}, 2160 cm^{-1}; TlL_3^{3-}, 2162 cm^{-1}.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA

The Reaction of Pentacyanonitrosylferrate(II) with Bases. III. Propanone–, Butanone–, and 3-Pentanone–Hydroxide Solutions

BY JAMES H. SWINEHART AND WILLFRED G. SCHMIDT

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An investigation of the reactions between aqueous propanone, butanone, and 3-pentanone solutions, containing hydroxide, and pentacyanonitrosylferrate(II) (nitroprusside), $(NC)_5FeNO^{2-}$, is described. In the case of propanone the rate law for the formation of the initial product, $(NC)_5Fe(C_3H_5NO_2)^{3-} = A$, is $k[(NC)_5FeNO^{2-}][OH^-][\text{propanone}]$, where k is 0.39 M^{-2} sec^{-1} at 297°K and $\mu = 1.0$ (NaCl and NaOH). The aquation of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ is first order in the iron-containing species and yields $(NC)_5FeH_2O^{3-}$ and $CH_3C(=O)CH=NOH$ as the products. The first-order rate constant for this process is $(1.50 \pm 0.10) \times 10^{-2}$ sec^{-1} at 298°K and $\Delta H^{\ddagger}$ is 17.8 ± 0.5 kcal/mole. The reactions between aqueous 3-pentanone and butanone solutions, containing hydroxide, and pentacyanonitrosylferrate(II) lead to the formation of species which are the 3-pentanone and butanone analogs of $(NC)_5Fe(C_3H_5NO_2)^{3-}$. The aquation reaction for these species, A, follows the rate law $-d[A]/dt = k_2[OH^-][A] + k_3[OH^-][\text{ketone}][A]$. The products are $(NC)_5FeH_2O^{3-}$ and the isonitroso derivative of the corresponding ketone. For the 3-pentanone system $k_2 = 0.50 \pm 0.03$ M^{-1} sec^{-1} at 298°K. The enthalpy of activation, $\Delta H^{\ddagger}$, is 8.8 ± 0.4 kcal/mole and $\Delta S^{\ddagger}$ is -30 ± 2 eu. The enthalpy of activation for k_3 is 5.0 ± 0.3 kcal/mole, and k_3 equals 8.4 ± 0.3 M^{-2} sec^{-1} at 298°K. The rate constants k_2 and k_3 at 298°K in the butanone system are 0.65 M^{-1} sec^{-1} and 3.3 M^{-2} sec^{-1}.

Introduction

Reactions in aqueous solution between pentacyanonitrosylferrate(II) (nitroprusside), $(NC)_5FeNO^{2-}$, and ketones and aldehydes containing acidic methylene groups are well known.[1] Recently complete kinetic studies of the hydroxide-[2] and hydrogen sulfide-

[1] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p 1345.

[2] J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).