agreement was found between the amount of $Ni(CO)_4$ that reacted and the NO_2^- formed. The presence of NO_2^- was also confirmed by the isolation of $NiNO_2NO[(C_6H_5)_3P]_2$ from the reaction of triphenylphosphine with these blue materials. Some material is always formed (5–10%) which is unreactive with cyclopentadiene. Its composition could not be determined but seemed to consist of Ni(II), NO_2^-, OH^-, and $N_2O_2^{2-}$.

The results of an experiment which was identical with (5) above are shown in Fig. 2. These results were obtained by taking several small samples of the gas in the autoclave during the course of the reaction. It was difficult to get many gas samples when only a little of the nickel carbonyl had reacted since 50% reacted within 1 min. Considering the analytical difficulties, these results closely correspond to eq. 1.

The results obtained in cyclohexane and ethanol show that the solvent plays no role in the reaction (eq. 1). The only difference in the products obtained in cyclohexane and ethanol is due to solvation. In ethanol, the product is solvated and soluble but the product is not solvated or soluble in cyclohexane. The compound which is obtained from cyclohexane analyzed reasonably well for $Ni(NO_2)(NO)$ and its infrared spectrum shows that it is definitely a nitrosyl. Due to its reactivity the compound was not further characterized. It undoubtedly has a structure more complex than the simple monomer. Its nitrosyl frequency at 1845 cm.$^{-1}$ along with its composition suggest that it is similar to the nitrosyl nickel halides $(NiBrNO)_x$ described by Jahn and Hieber.[10] It has been reported[8] that solutions of this compound in alcohol are unstable. However, our experience has shown that when oxygen and/or water are absolutely excluded these blue solutions can be kept for months without change, but when exposed to traces of water or oxygen they decompose rapidly.

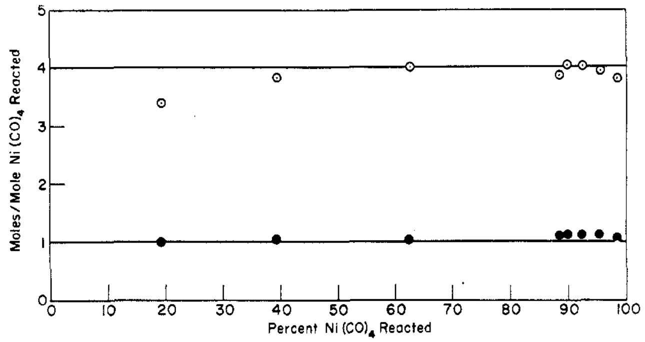

Fig. 2.—Experimental points and calculated values for the reaction of NO with $Ni(CO)_4$: —•— represents the theoretical values according to eq. 1 or eq. 3; ⊙ represents the experimental results for NO; ● represents the experimental results for N_2O.

Conclusions

When nickel carbonyl is treated with nitric oxide at superatmospheric pressure the compound $Ni(NO_2)(NO)$ is almost exclusively obtained. This is a mononitrosyl similar to those previously obtained from the reaction between nitric oxide and dicarbonylbis(triphenylphosphine)nickel.[5] Thus the only nitrosyl nickel complexes which result from the reactions between Ni(0) complexes and nitric oxide are of the type $[NiNO]^+$.

Acknowledgment.—The authors thank Earle Hewitt for his experimental assistance and the Physical Measurements group of this Institute for the chromatographic analyses.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Metal Derivatives of Arylazopyrazolone Compounds. VI. Molarity Quotients of Azo Derivatives of 1-Phenyl-3-methyl-5-thiopyrazolone

BY FRED A. SNAVELY, WALTER S. TRAHANOVSKY,[1] AND FRED H. SUYDAM

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The relative formation constants of the metal derivatives of some azo derivatives of 1-phenyl-3-methyl-5-thiopyrazolone have been measured in 75 vol. % dioxane. The decreasing order of stability (K_1) for the bivalent derivatives of 1-phenyl-3-methyl-4-benzeneazo-5-thiopyrazolone is Cu > Ni > Cd > Co > Zn, which compares with Cu > Ni > Co > Zn for the analogous derivative of 5-pyrazolone. The azothiopyrazolones show a stronger affinity for metal ions than their oxygen analogs. Infrared and chemical data favor a thiopyrazolone structure for the azo derivatives analogous to the azopyrazolone structure for the 5-pyrazolone series. The C═S peak for the chelating agents is assigned from 1240 to 1200 cm.$^{-1}$. Metal derivatives were prepared and characterized.

Introduction

This report is a continuation of our study on the relative bonding of oxygen, sulfur, and nitrogen to metal ions. Recently we reported data[2,3] on the relative coordination affinities of oxygen-, sulfur-, and nitrogen-containing chelating agents in which methoxy,

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[1] Summer Research Fellow, Franklin and Marshall College, 1960.

[2] F. A. Snavely and G. C. Craver, *Inorg. Chem.*, **1**, 890 (1962).

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Table I

Chelate Formation Constants for the Azothiopyrazolones in 75% Dioxane at 30°

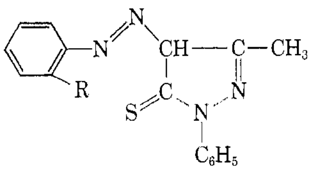
pK_D	Metal ion	log K_1[a]	log K_2[a]	log K_{av} at $\bar{n}$ = 1
1-Phenyl-3-methyl-4-(benzeneazo)-5-thiopyrazolone				
10.74	Cu(II)	>13	...	...
	Ni(II)	10.80 ± 0.18	9.75 ± 0.17	10.28
		10.70	9.88	
	Cd(II)	7.60 ± 0.07	9.06 ± 0.04	8.33
		7.56	9.06	
	Co(II)	7.09 ± 0.06	9.34 ± 0.12	8.22
		7.08	9.35	
	Zn(II)	6.59 ± 0.14	9.46 ± 0.17	8.02
		6.48	9.55	
	Pb(II)	...	...	~7.8
1-Phenyl-3-methyl-4-(2-methoxybenzeneazo)-5-thiopyrazolone				
12.00	Cu(II)	>13	...	...
	Ni(II)	11.56 ± 0.05	10.25 ± 0.11	10.91
		11.63	10.18	
	Co(II)	11.29 ± 0.14	10.23 ± 0.28	10.73
		11.32	10.32	
	Cd(II)	8.78 ± 0.08	9.93 ± 0.14	9.35
		8.74	9.88	
	Zn(II)	8.21 ± 0.12	9.23 ± 0.22	8.72
		8.42	9.06	
1-Phenyl-3-methyl-4-(2-thiomethoxybenzeneazo)-5-thiopyrazolone				
10.70	Ni(II)	9.45 ± 0.20	10.31 ± 0.18	9.90
		9.30	10.49	
	Cd(II)	8.36 ± 0.07	8.94 ± 0.09	8.63
		8.38	8.92	
	Pb(II)	7.81 ± 0.11	8.58 ± 0.14	8.20
		8.01	8.48	
	Zn(II)	6.61 ± 0.18	7.68 ± 0.20	7.15
		6.47	7.83	

[a] The first set of constants was calculated by the Block and McIntyre method,[8] the second set by the Irving and Rossotti method 5.[9]

thiomethoxy, and tertiary nitrogen bonds were involved.

The inert gas type ions, zinc(II), and the uranyl ion bonded more strongly with the oxygen derivatives, while the transition metal ions and cadmium(II) bonded more strongly with the sulfur-containing derivatives. This is in agreement with the limited data available on sulfur and oxygen bonding to metal ions.[4]

Because arylazothiopyrazolone compounds give an excellent vehicle for further comparison of oxygen and sulfur bonding, the following compounds were prepared and studied. These compounds are quite stable and copper–mercapto bonds can be studied without the oxidation to disulfides that plagues the study of other mercaptans.



I, R = H
II, R = OCH_3
III, R = SCH_3

Experimental

Preparation of Azo Compounds.—The 1-phenyl-3-methyl-5-thiopyrazolone was prepared by the method of Michaelis and was recrystallized from 95% ethanol, m.p. 110–111°, lit.[5] 109°.

1-Phenyl-3-methyl-4-benzeneazo-5-thiopyrazolone.—To 500 ml. of water which contained 33 g. of sodium acetate trihydrate and 5 g. of sodium hydroxide was added 3.8 g. of 1-phenyl-3-methyl-5-thiopyrazolone. To this solution, cooled to 5°, benzene diazonium chloride was slowly added with stirring. After standing for 2 hr., the red solution was made acid with hydrochloric acid, and the crude red precipitate was filtered, washed with hot water, and recrystallized from 95% ethanol to give 3.8 g., 64% yield, of dark red needles, m.p. 97–98°, lit.[5] 97°.

The 1-phenyl-3-methyl-4-(2-methoxybenzeneazo)-5-thiopyrazolone was prepared in an analogous manner and recrystallized from 95% ethanol to give dark red needles with a greenish reflectance, m.p. 133–134°.

Anal. Calcd. for $C_{17}H_{16}N_4OS$: C, 63.13; H, 4.98; N, 17.33. Found: C, 62.70; H, 5.14; N, 16.75.

The 1-phenyl-3-methyl-4-(2-thiomethoxybenzeneazo)-5-thiopyrazolone was prepared in an analogous manner and recrystallized from 95% alcohol to give dark red needles with a greenish reflectance, m.p. 120–121°.

Anal. Calcd. for $C_{17}H_{16}N_4S_2$: C, 60.11; H, 4.75; N, 16.50. Found: C, 60.19; H, 4.68; N, 16.38.

The S-methyl derivative of 1-phenyl-3-methyl-4-benzeneazo-5-thiopyrazolone was prepared by the method of Michaelis and was recrystallized from 95% alcohol, m.p. 61–62°, lit.[6] 63°.

Preparation of Metal Derivatives.—In 100 ml. of 75% dioxane under nitrogen were dissolved 1 mmole of the azo compound and 0.5 mmole of the metal nitrate. Dilute sodium hydroxide was slowly added with stirring to a meter reading which corresponds to the mid-point of the formation buffer zone of the complex. After standing, the metal derivatives precipitated out, copper(II), lead(II), and cobalt(II) almost instantly.

The derivatives were suction filtered, washed with cold 75% dioxane, and dried in a vacuum desiccator. The metal derivatives were analyzed without further purification.

Analysis.—Microanalyses by Dr. G. Weiler and Dr. G. B. Strauss, Oxford, England.

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.[7] The solutions were so adjusted that in 100 ml. of solution there were 1.00 mmole of chelating agent, 0.996 mmole of nitric acid, and 0.200 mmole of metal nitrate. The titrant was 1.001 N carbonate-free sodium hydroxide. The meter reading correction factor (log U_H) equals 0.47. Titration time was about 2 hr.; nickel(II) titrations required about 25 hr.

Calculations.—The molarity quotients for the reactions $Cu^{+2} + Ch^- = CuCh^+$ and $CuCh^+ + Ch^- = CuCh_2$ were calculated by the method of Block and McIntyre.[8] The constants were also calculated graphically by plotting $\bar{n}/(1 - \bar{n})a$ against $(\bar{n} - 2)a/(1 - \bar{n})$, where a is the concentration of the anionic species of the ligand and $\bar{n}$ the average number of ligand molecules bound per metal ion. The slope and intercept of this linear plot are equal to K_1K_2 and K_1, respectively.[9]

Results

The pK_D values of the chelating agents for the reaction $HCh = H^+ + Ch^-$ are recorded in Table I. The log of the formation constants recorded in Table I are the average of at least four sets of calculations from experimentally determined points. The two different

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[8] B. P. Block and G. H. McIntyre, Jr., *ibid.*, **75**, 5667 (1953).

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TABLE II

PHYSICAL PROPERTIES OF METAL DERIVATIVES, 2:1, AZO COMPOUND TO METAL ION

Metal derivatives	Color of crystals	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
			Compound I					
Cu	Black	244–245	59.10	58.71	4.03	3.88	17.23	17.10
Ni	Brown	233–234	59.52	58.98	4.03	4.12	17.36	16.95
Co	Black	245–246	59.52	59.55	4.06	3.78	17.35	17.52
Zn	Red-orange	232–233	58.93	56.63	4.02	4.36	17.18	17.20
Cd	Red-orange	268–269	54.97	55.10	3.74	3.68	16.02	16.00
Pb	Orange	282–283	48.41	48.46	3.30	3.18	14.11	14.25
			Compound II					
Cu	Black	224–225	58.29	57.48	4.25	4.26	[a]	
Ni	Black	242–243	57.87	57.80	4.26	4.42	15.74	15.88
Zn	Red-orange	250–252	57.38	57.47	4.23	4.43	15.75	15.71
Cd	Red-orange	261–262	53.82	53.94	3.96	3.97	14.77	14.45
			Compound III					
Ni	Black	238–239	55.36	55.65	4.07	4.91	15.20	17.20[b]
Co	Black	>300	55.34	55.52	4.06	3.97	15.18	15.38

[a] Insufficient material for a nitrogen determination. [b] A second sample gave 14.10% nitrogen.

methods of calculating the constants give results that are in good agreement.

The formation constants for the copper(II) titrations could not be calculated because, for all three azo compounds, the reaction was complete before the addition of sodium hydroxide. The titrations with copper(II) and cobalt(II) were erratic unless performed under nitrogen and were not reproducible with the *o*-SCH$_3$ compound even under nitrogen. With the other metal ions the results with or without a nitrogen atmosphere were identical.

No values are reported for lead(II) and the *o*-OCH$_3$ compound since a precipitate formed before the end of the titration. The value recorded for lead(II) and the plain azo derivative, compound I, is only approximate, as coordination occurred within the buffer zone of hydroxide formation. Titrations with manganese-(II), magnesium(II), beryllium(II), and the uranyl ion resulted in hydroxide formation.

The decreasing stability order for the simple bidentate azothiopyrazolone, compound I (log K_1), is Cu > Ni > Cd > Co > Zn. There are variations for the other two azo compounds, but in all examples cadmium is significantly more stable than zinc. For most of the metal derivatives it is found that $K_2 > K_1$, as noted with the analogous oxygen derivatives.[3,7]

The 2:1 metal derivatives and their elemental analyses are listed in Table II. The copper derivative of the *o*-SCH$_3$ compound and the cobalt derivative of the *o*-OCH$_3$ compound were not of constant composition.

Chemically the chelating agents are resistant to oxidation in acid solutions, but they are slowly converted to the disulfides in basic solution in the presence of air oxygen. However, in the absence of air oxygen they are stable in basic solution and can be recovered unchanged by the addition of excess acid.

Discussion

The unsubstituted benzeneazo-5-thiopyrazolone, a bidentate ligand, is the best of the three chelating agents to use for a comparison with the benzeneazo-5-pyrazolones. There are certainly fewer steric factors than found with the terdentate ligands. It is reported[10] that 1-phenyl-3-methyl-4-(3-chlorobenzeneazo)-5-pyrazolone (as well as other azo-5-pyrazolone derivatives) coordinates with bivalent metal ions in the following decreasing order for K_1 and K_{av}: Cu > Ni > Co > Zn. The simple azothiopyrazolone compound shows the following order: (K_{av}) Cu > Ni > Cd > Co > Zn > Pb and (K_1) Cu > Ni > Cd > Co > Zn. With all four metal ions the stability constants are significantly greater for the thio derivative, with cobalt(II) and zinc-(II) showing the smallest increase. With essentially equal basicity of the two chelate anions, the increased stability of the metal derivatives of the sulfur compound shows the sulfur to bond more strongly than the oxygen. It is also significant that cadmium(II) and lead(II) show a strong affinity for sulfur; these two cations did not form compounds with the simple oxygen derivatives.

A comparison of oxygen and sulfur bonding becomes less valid with the *o*-OCH$_3$ and *o*-SCH$_3$ compounds due to the greater possible steric effects. The terdentate nature of the methoxy compound is apparent in that log $K_1 >$ log K_2 for the nickel and cobalt derivatives. The metal derivatives of the methoxy compound are also more stable than those of the simple azothiopyrazolone or than the metal derivatives of *o*-methoxybenzeneazo-5-pyrazolone oxygen.[3] It is interesting that zinc forms a less stable derivative with the *o*-SCH$_3$ compound than with the other two azothiopyrazolones.

It is rather surprising that the nickel derivative of the *o*-SCH$_3$ compound shows log $K_2 >$ log K_1. In addition the log K_1 and log K_{av} are less than for the *o*-thiomethoxy derivative of the 5-pyrazolone.[3] Molecular models show that the two sulfur atoms are so bulky that it is probably impossible for the terdentate

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(10) F. A. Snavely and B. D. Krecker, *J. Am. Chem. Soc.*, **81**, 4199 (1959).

molecule to assume a planar configuration around the nickel in the 1:1 complex.

Infrared spectra of the three chelating agents give no evidence of an SH stretch. The azothiopyrazolones do show a wide absorption band (1240–1200 cm.$^{-1}$) in the region which has been suggested as representing the C=S bond.[11] This band disappears in the metal derivatives as well as the band at 1560 to 1555 cm.$^{-1}$ which was called a possible N=N stretch.[12] The band at 1240–1200 cm.$^{-1}$ also disappears in the S-methyl derivative of 1-phenyl-3-methyl-4-phenylazo-5-thiopyrazolone. The lack of SH stretch is not surprising since, like the analogous oxygen compounds, this would require the enolization of what could be considered a cyclic thioamide.

A new, strong, multipeaked absorption is found in the metal derivatives in the region 1470–1350 cm.$^{-1}$ which corresponds to the reported[12] broad absorption for the copper derivatives of the analogous oxygen derivatives at 1470–1385 cm.$^{-1}$. This multipeaked absorption is also present in the S-methyl derivative of compound I. The most intense band in this region is at lower frequencies than found in the metal derivatives of the oxygen compounds. This multi-peaked absorption is probably due to the pyrazole ring vibration.

Acknowledgment.—The authors are indebted to the National Science Foundation (NSF-G12306) for financial support in carrying out this investigation.

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Contribution from the Los Alamos Scientific Laboratory,
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Fluoride Complexes of Pentavalent Uranium[1]

By R. A. PENNEMAN, G. D. STURGEON, and L. B. ASPREY

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Solid fluoride complexes of pentavalent uranium are formed by heating UF_5 with ammonium or alkali fluorides under anhydrous conditions. A series of complexes having $MF:UF_5$ ratios (M = NH_4, Li, Na, K, Rb, and Cs) of 1:1, 2:1 (except Li and Na), and 3:1 (except Li) were characterized by X-ray powder diffraction. These white to pale blue compounds exhibit characteristic absorption in the 1.3 to 1.5 μ region.

Introduction

We reported in a brief communication that UF_5 reacts under anhydrous conditions with NH_4F or alkali fluorides to form complex fluorides of the form MUF_6.[2] That work has been extended and herein we report the synthesis of a series of compounds of pentavalent uranium as well as their X-ray powder diffraction data and spectra.

There are only three cases of elements having a 5f^1 electronic configuration in chemically tractable valence states: *i.e.*, Pa(IV), U(V), and Np(VI). Additions to the few data on U(V) are of chemical interest as well as having theoretical importance since U(V) absorption spectra in particular can often be interpreted relatively simply.[3]

Few fluoride complexes of U(V) have been characterized previously. Uranium hexafluoride is reduced by NH_3 under certain conditions to give NH_4UF_6[4] and by NO to give $NOUF_6$.[5] Note that Galkin, *et al.*,[6] report that reduction of UF_6 by NH_3 gives UF_5 and a complex of *tetravalent* uranium, NH_4UF_5. Ruedorff and Leutner[7] prepared Na_3UF_8 (contaminated with NaF) from trisodium uranium(IV) fluoride by fluorination at carefully controlled temperatures. However, they could not prepare the analogous potassium uranium(V) compound, but instead always obtained a compound containing U(VI).

A more general approach than either of the above is one which starts with UF_5 and is the one used in this study. All alkali fluorides were found to react with UF_5 to produce complex fluorides containing uranium(V).

Experimental

Materials.—Reagent grade NH_4F, LiF, NaF, and KF were used. Anhydrous UF_6 was distilled. Certified uranium tetrafluoride (99.9%), RbF (99.7%), and CsF (99.7%) were used. The UF_5 was prepared by treatment of UF_4 with gaseous UF_6 in a nickel reactor under anhydrous conditions. Specially prepared UF_4 of high surface area[8] reacted smoothly with UF_6 at 80–100° to yield β-UF_5. Increase in the temperature to 200° yielded α-UF_5. Both forms of UF_5 had the theoretical weight composition

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

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