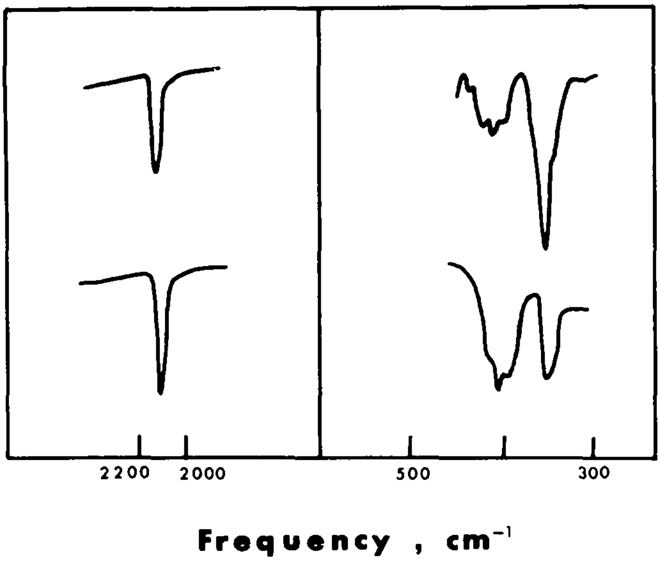

Fig. 1. Infrared spectra of $(C_6H_5)_4As[Re(CN)_6]$ (upper) and $C_4H_9N[Re(CN)_6]$ (lower).

The visible and u.v. spectrum of $(C_6H_5)_4As[Re(CN)_6]\cdot H_2O$ exhibits maxima at 26,600 cm^{-1}, 23,800 cm^{-1} and 18,200 cm^{-1}. The two higher energy bands have extinction coefficients greater than 10^3, while the band at 18,200 cm^{-1} is about half as intense as the higher lying bands. These are probably all charge transfer bands.

We could not determine definitely if the water present is coordinated; both the O–H stretching and H–O–H bending modes were very broad, and other modes could not be seen. The actual coordination geometry of this hexacyanide is uncertain.

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Molarity quotients of the metal derivatives of arylazopyrazolidinediones

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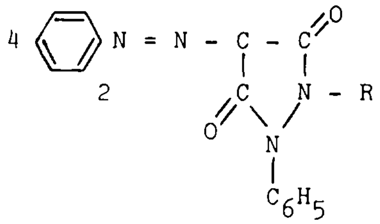
AS A CONTINUATION of our study of the coordination of arylazopyrazolone compounds, we have prepared a series of azo derivatives of the pyrazolidine-diones and studied their coordination with divalent metal ions.

The molarity quotients are listed in Table 1, and the acid dissociation constants are listed in Table 2. The behavior of the 1,2-diphenyl-4-phenylazo-3,5-pyrazolidinediones with metal ions is like that of the azo-5-pyrazolones[1] with 3 : 1 coordination observed with nickel(II) and cobalt(II) and with zinc coordinating within the buffer zone of hydroxide formation leading to a precipitate of zinc hydroxide. The 2-OCH_3 and 2-SCH_3 compounds are terdentate ligands and again show that divalent

[1] F. A. Snavely, W. C. Fernelius and B. P. Block, *J. Am. chem. Soc.* **79**, 1028 (1957); F. A. Snavely and B. D. Krecker, *J. Am. chem. Soc.* **81**, 4199 (1959).



Where R = H or C_6H_5

copper, nickel, cobalt, and cadmium bond more strongly to sulfur while zinc bonds more strongly to the oxygen derivative [2].

Table 1. Formation constants for metal derivatives of the azo-1,2-diphenyl-3,5-pyrazolidinediones at 30°C in 75/25 dioxane-water

Azo compound	Metal	log K_1	log K_2‡	log K_3
4-F	Cu	6·86 ± 0·11	7·51	
	Ni	5·25 ± 0·38	6·48	5·20
	Co	5·05 ± 0·31	5·54	4·74
4-Br	Cu	6·90 ± 0·10	7·47	
	Ni	5·44 ± 0·24	6·20	5·03
	Co	4·84 ± 0·10	5·65	4·60
4-Cl	Cu	7·01 ± 0·08	7·31	
	Ni	5·75 ± 0·15	5·92	
	Co	4·90 ± 0·17	5·30	
4-OCH_3	Cu	7·23 ± 0·08	7·84	
	Ni	5·50 ± 0·22	6·43	4·60
	Co	5·13 ± 0·18	5·60	4·31
4-H	Cu	7·30 ± 0·09	7·45	
	Ni	5·22 ± 0·11	6·44	4·51
	Co	4·73 ± 0·29	5·64	4·17
4-CH_3	Cu	7·29 ± 0·14	7·85	
	Ni	5·53 ± 0·20	6·53	4·60
	Co	4·75 ± 0·28	5·97	3·99
2-Cl*	Cu	7·23 ± 0·16	8·48	
2-OCH_3	Cu	8·84 ± 0·04	8·57	
	Ni	7·76 ± 0·06	6·90	
	Co	6·61 ± 0·06	6·12	
	Zn	5·91 ± 0·16	6·00	
	Cd	4·90 ± 0·02	5·08	
2-SCH_3	Cu	> 11.	8·35†	
	Ni	9·78 ± 0·15	9·00	
	Co	7·35 ± 0·19	8·47	
	Zn	5·66 ± 0·13	6·03	
	Cd	5·56 ± 0·10	6·04	

*Nickel and cobalt coordinate within the buffer zone of hydroxide formation.

†Taken from the formation curve at $\bar{n} = 1·50$.

‡Uncertainty in log K_2 no greater than in log K_1.

2. F. A. Snavely, C. H. Yoder and F. H. Suydam, *Inorg. Chem.* **2**, 708 (1963).

Table 2. Acid dissociation constants for the azo derivatives of the pyrazolidinediones at 30°C in 75/25 dioxane-water

R = C_6H_6	m.p.* (°C)	pK_D
4–F	189–91	9·07
4–Br	236–38	9·10
4–Cl	239–41	9·13
4–OCH_3	202–03	9·56
4–H	180–82	9·63
4–CH_3	158–60	9·81
2–Cl	177–78	10·02
2–OCH_3	179–80	10·01
2–SCH_3	179–80	10·29
R = H		
4–Cl	265–66	7·34
4–Br	273–75	7·47
4–H	232–33†	7·78
4–OCH_3	237–39	8·08

*Uncorrected.

†Rpt. [4] 232°.

No formation constants are reported for the 1-phenyl-4-phenylazo-3,5-pyrazolidinediones. Although only a single proton per molecule was titratable in the pK_D determination, titrations in the presence of metal ions showed an overall stoichiometry of more than one proton per molecule. There was no evidence for hydrolysis; a possible interpretation is that first $M(HCh)_2$ is formed followed by the removal of a proton to form $M(Ch)_2^-$. (Where H_2Ch represents the chelating agent, the second acidic proton coming from the ring NH group). However, back titrations with nitric acid did not always yield the original azo compound. Numerous titrations in which different ratios of chelating agent to metal ion were used did not yield a solution to the problem.

A few metal derivatives of the above compounds were isolated. Their elemental analysis is reported in Table 3. Magnetic data will be reported in a later publication.

EXPERIMENTAL

Preparation of compounds. The 1,2-diphenyl-3,5-pyrazolidinedione was prepared by adding 10 g of sodium metal to 300 ml of dry *n*-butanol, then adding 80 g of hydrazobenzene and 60 g of diethylmalonate. This mixture was refluxed for 15 hr after which the alcohol was distilled off. The residue was dissolved in water, washed with ether, and acidified with dilute HCl. The precipitate was washed with water and crystallized from 95% ethanol as dense, white crystals, m.p. 178°, [3] 173·5°.

The 1-phenyl-3,5-pyrazolidinedione was prepared by using phenylhydrazine in place of hydrazobenzene, m.p. 192° [4], 192°.

The azo compounds were prepared by coupling the appropriate diazotized amines to the pyrazolidinediones dissolved in water containing an equivalent amount of sodium hydroxide with excess sodium acetate serving as a buffer. The azo derivatives were digested in dilute HCl and crystallized from either alcohol or dioxane. Purity of the compounds was determined by measuring the neutral equivalents which were all within 0·1 per cent of calculated values.

The metal derivatives were prepared by the following general methods.

3. H. Ruhkopf, *Ber.* 73, 820 (1940).
4. R. Burmeister and A. Michaelis, *Ber.* **29**, 1502 (1891).

Table 3. Metal derivatives of the azo compounds of 1,2-diphenyl-3,5-pyrazolidinedione*

Metal	Method	Azo compound	m.p.†† (°C)	Carbon %		Hydrogen %		Nitrogen %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu†	A	4-H	241–43	65·15	63·19	3·91	4·11	14·48	13·75
Cu†	A	4-Cl	247–49	59·82	57·97	3·35	3·83	13·29	12·85
Cu	A	2-SCH_3	270–73	60·99	61·15	3·96	4·31	12·93	12·90
Cu	A	2-OCH_3	285–87	63·33	62·33	4·11	4·42	13·44	13·39
Cu(1 : 1)‡	C	2-SCH_3	>300	52·80	52·88	3·42	3·53	11·19	11·35
Cu(1 : 1)‡	C	2-OCH_3	>300	54·55	56·24	3·54	4·11	11·57	11·20
Ni	B	2-OCH_3	>300	63·71	63·18	4·13	4·37	13·51	13·00
Ni	B	2-SCH_3	>300	61·33	61·18	3·98	4·11	13·00	12·89
$Ni(2H_2O)$§	A	4-H	>300	62·63	61·07	4·23	4·71	13·92	14·20
$Ni(2NH_3)$**	B	4-F	>300	60·09	60·32	4·08	4·50	16·68	16·33
Co	A	2-OCH_3	>300	63·70	63·89	4·13	4·38	13·51	13·33
Co	A	2-SCH_3	281–83	61·32	61·34	3·98	4·17	13·00	12·90

*Compounds reported are 2 : 1, azo compound to metal. Analytical data of G. Weiler and F. B. Strauss, Oxford, England.

†Two compounds were shown to contain water, 1·83 per cent for 4-H-Cu and 2·04 per cent for 4-Cl-Cu. Calculated carbon, hydrogen and nitrogen on this basis would be 63·95, 4·04 and 14·21 for 4-H-Cu and 58·57, 3·51 and 13·01 for 4-Cl-Cu.

‡Formula of compound is Cu(Ch)Cl, where Ch equals chelate ion. Chloride ion determination by the precipitation of silver chloride gave, calcd. for SCH_3, 7·1 per cent found 7·5 per cent calcd. for OCH_3, 7·3 per cent found 7·1 per cent.

§Formula for compound is $Ni(CH)_2(H_2O)_2$.

**Formula for compound is $Ni(Ch)_2(NH_3)_2$. Product isolated with excess ammonia in the solution.

††Uncorrected.

A. The azo compound is added to hot 95 per cent ethanol and slightly less than an equivalent amount of 1 N sodium hydroxide is added. Enough ethanol is used so that a solution results after the addition of the base. To the boiling solution the correct amount of 1 M metal nitrate solution is added dropwise with stirring. In most cases the metal derivative precipitates within a few min and is filtered, washed with cold ethanol and dried at room temperature.

B. To a 50–50 mixture of 1 M metal nitrate solution and 95 per cent ethanol, concentrated aqueous ammonia is added in excess to form the ammine complex. The ammine complex is added dropwise to the boiling solution of the azo compound in 95 per cent ethanol. This solution is refluxed for 10–20 hr until ammonia is no longer liberated. The precipitate is filtered hot, washed with ethanol and dried at room temperature.

C. The 1 : 1, azo compound to metal, derivatives were prepared by this method. The azo compound is dissolved in hot ethanol-dioxane-water (about 1 : 1 : 1). Enough potassium chloride is added to saturate the solution. The copper(II) chloride, dissolved in water, is added rapidly to the hot solution. The copper derivatives precipitated from this solution; the 2 : 1, azo compound to metal, derivatives rather than the 1 : 1 were obtained when nickel(II) chloride was used instead of copper(II) chloride. The copper derivatives were washed with water, 95 per cent ethanol, and dioxane. The metal derivatives along with carbon, hydrogen and nitrogen analysis are listed in Table 3.

Potentiometric titrations. The titrations were performed at 30·0 ± 0·1° in 75 per cent dioxane as described previously[5]. The method of calculating the stability constants and acid dissociation constants has already been reported[5]. A simple expansion of the computer program to include 3 : 1, azo compound to metal, coordination was necessary.

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5. F. A. Snavely, D. A. Sweigart, C. H. Yoder and A. Terzis, *Inorg. Chem.* 6 1831 (1967).