

Infrared Spectra of Metal Dithizonates

ARNE DYFVERMAN

*Government laboratory for forensic chemistry (Statens rättskemiska laboratorium),
Stockholm 60, Sweden*

Solid phase infrared spectra of a number of dithizonates were recorded. They were found to be of four different types:

1. Dithizone.
2. Primary dithizonates of Ni²⁺, Pd²⁺, Pt²⁺, and Co.
3. Secondary copper(II) dithizonate.
4. Primary dithizonates of Au³⁺, Ag⁺, Hg²⁺, Tl⁺, Cu²⁺, Zn²⁺, Cd²⁺, In³⁺, Pb²⁺ and Bi³⁺.

This indicates, that the two groups of primary dithizonates may have different structures.

Dithizone (diphenylthiocarbazone; C₆H₅·N=N·CS·NH·NH·C₆H₅; HDz) has become of great importance as a reagent for the determination of heavy metals. At least 18 metals give chelate compounds with dithizone, but some of them are very unstable. Primary and secondary dithizonates are known. The primary dithizonates, *e.g.* Hg^{II}Dz₂ or Ag^IDz, are the most important. About seven metals also give secondary dithizonates, such as Cu^{II}Dz.

The structure of crystalline mercury dithizonate was elucidated by Harding,¹ but the structures of other metal dithizonates are still largely unknown. Irving and Cox² compared absorption spectra, in the visible region, of several dithizone complexes in carbon tetrachloride and found, that the complexes of nickel, palladium, platinum and gold gave spectra, which differed from those of other dithizonates. They pointed out, that the configuration of the ligand is probably not the same for all dithizonates.

To throw further light on this problem, infrared spectra of metal dithizonates were recorded. The purpose of this work was also to facilitate the identification of small amounts of metals, *e.g.* in toxicology. As the chelates are only sparingly soluble in organic solvents, solid phase spectra of dithizonates were prepared by the potassium bromide disk method. The N—H stretching frequencies around 3200 cm⁻¹ for dithizone and the dithizonates of Cu, Hg, and Co have previously been studied by Duncan and Thomas,³ but other records were not found in the literature.

EXPERIMENTAL

Reagents. Glass-distilled water and chloroform were used, also for the preparation of reagents and solutions. The chemicals were of analytical grade when obtainable.

Dithizone solution. A purified solution of dithizone in chloroform was prepared in the following way: Dithizone (0.2 g) in chloroform (100 ml) was shaken with dilute ammonium hydroxide (1 + 20, 200 ml). The water phase was filtered, acidified with dilute sulphuric acid and shaken with chloroform (200 ml). The organic phase was separated and diluted with another 200 ml of chloroform. The solution was stored in the refrigerator under a layer of sulphurous acid of the following composition: water (400 ml) + $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ (40 g) + H_2SO_4 (5 N, 50 ml). The dithizone solution thus prepared was 1.75 mM. The molarity was determined by extractive titration of a silver nitrate solution (0.01 N, 5 ml) as described by Iwantscheff,⁴ p. 71.

Instruments. A Hilger H 800 recording infrared spectrophotometer with double-beam operation and NaCl optics was used to obtain spectra between 4000 and 650 cm^{-1} . The slit width at 4000 cm^{-1} was set at 0.15 mm, the auto slit width control at 35 and the cam speed at 22.5 min/rev. 13 mm potassium bromide disks were pressed at 12 tons in a vacuum disk-press model 8 and hydraulic press PW 20 from Paul Weber, Stuttgart.

Preparations. In the following one equivalent of a metal is considered as the amount of metal, that binds one molecule of dithizone and one equivalent of dithizonate as the amount of a dithizonate, that contains one molecule of dithizone. The preparation of one dithizonate (NiDz_2) will be described first, as an example.

In a separatory funnel ammonium hydroxide (2 + 100, 50 ml), hydroxylamine sulphate (1 M, 2 ml), chloroform (38.5 ml), dithizone solution (11.5 ml; 20 μmole dithizone) and nickel sulphate solution (1 mg Ni/ml, 1 ml; 34 $\mu\text{equiv. Ni}$) were mixed. After shaking the funnel for 1 min the colour of the extract was brownish black. A further addition of the nickel standard (1 ml) was made and the funnel shaken again. No colour changes occurred. The chloroform extract was separated and washed 3 times by shaking with ammonium hydroxide (2 + 100, 50 ml), 15 sec each time.

The extract was dried over sodium chloride and aliquots (2.5, 5, and 10 ml, corresponding to 1, 2 and 4 $\mu\text{equiv.}$ of NiDz_2 , respectively) were added into three glass dishes, containing 0.4 g of potassium bromide (ignited and kept over P_2O_5).

The dishes were placed overnight in a ventilated, dark compartment at 35°C, where the chloroform evaporated. The residues were thereafter dried for one or two days in vacuum over P_2O_5 . The mixture of potassium bromide and dithizonate was now very carefully pulverised in an agate mortar and dried once more in the same way. The bromide disks were then pressed and preserved over P_2O_5 .

The other dithizonates were prepared similarly. The reagents and solutions used are compiled in Table 1, columns 2–8. The metal salt solutions as a rule contained either 1 mg or 10 $\mu\text{equiv.}$ of metal per ml. Some of them had to be acid, but the amount of acid introduced did not significantly alter the pH of the mixtures, unless mentioned in column 4.

The extractions were made from either acid or alkaline solutions (shaking time 2 min). The "acid" extracts were washed 3 times with water (50 ml) and the "alkaline" extracts 3 times with ammonium hydroxide (2 + 100, 50 ml). Three disks, usually containing 1, 2, and 4 $\mu\text{equiv.}$ of dithizonate, respectively, were prepared from each extract.

Blanks were made in nearly all experiments. They were prepared in the same way, except that the metals were not added. Blanks from acid mixtures (Table 1, col. 2–8) were used to obtain dithizone spectra. In the blanks from alkaline mixtures, dithizone was removed when the extracts were washed with ammonium hydroxide. Daylight was kept out during the preparative work.

The preparation of tin dithizonate was attempted, but the product could not be investigated because it decomposed too rapidly. Of two secondary dithizonates prepared (Table 1), one (Cu^{2+}) gave usable infrared spectra. The secondary palladium, platinum, and silver dithizonates are too slightly soluble in organic solvents to be prepared in the manner, described in this paper.

Spectra in the visible region. Aliquots of extracts, which had been prepared from acid solutions, were diluted with chloroform. Extracts from alkaline solutions were diluted with ammoniacal chloroform to prevent decomposition (chloroform was shaken with ammonium hydroxide, 2 + 100, and then dried over NaCl). Visible absorption spectra

Table 1. Preparation and properties of dithizonates.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Metal	Water, ml	Ammonium hydroxide, 2 + 100, ml	Other additions	Hydroxylamine sul- phate M, ml	Chloroform, ml	Dithizone solution, ml	Metal, μ equiv.	Excess of dithizone, %	Excess of metal, %	Dithizone, μ equiv./ml extract	Colour of extract	Absorption max. of extract, m μ	Absorption max. of dithizone from disk	Signs of change in disk	Signs of decomposition during measurement	Agreement with Iwantschew ⁴	Other remarks
Ni ²⁺		50		2	38.5	11.5	68		240	0.4	br b	477, 555	476, 555 667	no	no	yes	
Pd ²⁺	25		a	2	38.5	11.5	35		75	0.4	gr g	487	448, 636 486	no	no	yes	
Pt ²⁺	10		c	3	44.3	5.7	30		200	0.2	g y	544	544	no	no	yes	
Co ³⁺ s		50		2	30	20	20	75	70	0.4	d r	458	453	no	yes	?	e
Co ³⁺ , sec.		50		2	38.5	11.5	34		150	0.4	d v r	448	448	yes	yes		t
Cu ²⁺ , sec.		50		3	38.5	11.5	50		90	0.4	y br	438, 570	438, 590	no	no	yes	
Au ³⁺	45		f	2	38.5	11.5	38		10	0.4	br d r	461	461	small	yes	no	i
Ag ⁺	25		h	3	38.5	11.5	22		400	0.4	y o	490	490	no	no	yes	
Hg ²⁺	100		k	3	50	20	100	large	0	0.4	r	503	507 (no)	no	no	yes	
Tl ⁺	50		m	3	38.5	11.5	20		0	0.4	d r v	545	545	no	yes		l
Cu ²⁺		50		3	33	17	20	48	0	0.4	r	529	529	no	no	yes	
Zn ²⁺		50		3	40	10	10	75	160	0.2	r	508	508	no	no	(yes)	
Cd ²⁺		50		2	38.5	11.5	52		31	0.4	r	511	513	no	slight	yes	
In ³⁺			n	3	35	15	20		185	0.4	r		492	no	no	yes	
Pb ²⁺	50		p	3	38.5	11.5	57			0.4	r			no	no	yes	
Bi ³⁺			n	2	38.5	11.5	57			0.4	r			no	no	yes	

a. HCl (0.4 mequiv.) from Pd solution. b. Black. br. Brown. c. HCl (3 N, 20 ml) + filtrate (5 ml) from SnCl₄·2H₂O (5 g) in HCl (3 N, 100 ml). d. Dark. e. Purity uncertain. f. H₂SO₄ (5 N, 1 ml). g. Green. gr. Gray. h. Acetic acid (1 ml). i. Small amount of dithizone present. k. Dithizone mixture s (296 ml). l. The extract was sensitive to dilution. Small changes in solution from the disk were probably due to dilution. m. Acetic acid (0.5 ml) + sodium acetate · 3H₂O (1.2 g). n. 50 ml of a solution containing NH₄OH (conc., 10 ml/l) and KCN (5 g/l). o. Orange. p. NH₄OH (conc., 10 ml). r. Red. s. Duncan and Thomas³ reported, that Co³⁺ is probably air oxidised to Co³⁺ when the dithizonate is formed. t. The infrared spectrum indicated a mixture. v. Violet. y. Yellow.

Table 2. Infrared spectra of dithizone, secondary copper dithizonate and four primary dithizonates.

Peak No.	Dithizone	Peak No.	Ni ²⁺	Pd ²⁺	Pt ²⁺	Co ²⁺ + a	Peak No.	Cu ²⁺ , secondary
1	~3040	1	3220	3	3240	3150	1	>3000
2	1590	2	3030	w	3045	3050	2	1582
3	~1515	3	1593	16	1594	1597	3	1476
4	1500	4	1528	35	1527	1524	4	1455
5	~1485	5	1494	5	1494	1494	5	1338
6	1460	6	?	6	1473	1471	6	1317
7	1440	7	1453	3	1456	1454	7	1196
8	1381	8	1433	w	1434	1433	8	1168
9	~1330	9	1335	5	1336	1335	9	1148
10	1318	10	1335	48	1336	1335	10	1090
11	1249	11	1311	2	1311	1272	11	1018
12	1223	12	1283	17	1281	1272	12	994
13	1215	13	1223	66	1224	100	13	~960
14	1172	14	1215	66	1216	72	14	904
15	1146	15	1170	3	1170	3	15	874
16	1093	16	1100	8	1099	5	16	820
17	1068	17	1071	8	1071	8	17	757
18	~1020	18	1068	8	1071	8	18	~740
19	990	19	1025	2	1025	3	19	~715
20	970	20	997	3	997	3	20	~670
21	900	21	956	w	957	w	21	
22	888	22	934	4	937	8	22	
23	872	23	905	3	908	4	23	
24	825	24	885	2	886	2	24	
25	772	25	854	w	856	2	25	
26	756	26	831	w	830	w	26	
27	745	27	811	?	812	w	27	
28	709	28	784	3	780	4	28	
29	670	29	746	16	748	17	29	
		30	729	10	729	10	30	
		31	711	4	712	5	31	
		32	677	10	679	10	32	

The first column under each heading lists peak wave-numbers in cm^{-1} and the second peak absorption intensities in 100A/d, where A = absorbance and d = amount of dithizonate, micro-equivalents, in the potassium bromide disk.

a. See Table 1, note s. b. Broadening of peak 14. i. Inflection. o. Opaque. w. Weak.

Table 3. Infrared spectra of primary dithizonates.

Peak No.	Au ³⁺	Ag ⁺	Hg ²⁺	Tl ⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	In ³⁺	Pb ²⁺	Bi ³⁺
1										
2	w	3190	3240	3165	3190	3195	3205	3190	3200	3210
3	3040	1596	3050	3040	3045	3035	3045	3030	3040	3035
4	1598	10	1600	1599	1594	1593	1597	1594	1598	1597
5	1520	25	1526	1512	1516	1522	1525	1520	1520	1520
6	1500	i?	1497			1494	1495	1495	1496	1495
7	1457	13	1457	1457	1456	1459	1472	1455	1456	1480
8	1436	6	1436	1426	1429	1432	1433	1431	1431	1455
9	1384	10	1361	1351	1332	1339	1354	1337	1342	1433
10	1330	7	1310	1304	1303	1307	1311	1307	1342	1350
11	1256	17	1263	1259	1269	1275	1278	1269	1308	1306
12	1183	15	1189	1190	1202	1203	1203	1199	1268	1264
13	1152	10	1163	i	1184	1179	1177	1175	1200	1191
14	1125	19	1137	1124	broad	1150	1156	1145	1176	1174
15									1150	1162
16	1069	6	1071	1070	b	1072	1134	1070	1150	1144
17	1018	w	1021	1021	1070	?	1071	?	1071	1069
18									1022	1019
19	916	w	992	911	w	997	993	995	996	993
20									911	911
21	885	2	891	885	w	892	899	887	898	887
22	849	w	852	850	w	857	882	887	884	887
23									855	851
24	748	i	761	762	w	825	813	821	824	824
25									763	760
26									746	746
27	706	2	707	705	3	712	727	707	708	705
28	677	6	677	678	6	675	675	675	675	676

Explanatory notes. See under Table 2.

were read in a Beckman B spectrophotometer *vs.* chloroform (Table 1, col. 13). When the infrared records had been made, a part of one disk from each experiment was crushed in a centrifuge tube, containing chloroform or ammoniacal chloroform (*cf.* above). The solutions were filtered and the absorption spectra read again (Table 1, col. 14). The readings were repeated a few minutes later to see if changes occurred during the time these measurements were made (Table 1, col. 16). Comparisons between the spectra in col. 13 and 14 showed, that as a rule the substances had not changed markedly in the KBr disks (Table 1, col. 15).

The visible spectra in col. 14 (and 13) were compared with data in Iwantscheff's book ⁴ (Table 1, col. 17). The spectrum of the gold dithizonate did not agree with those data, but we believe that it was the primary gold dithizonate because (1) it was prepared from acid solution, which is known to favour the formation of primary dithizonates; (2) the infrared spectrum suggested that the product was a single compound; (3) the infrared spectrum resembled the spectra of a group of other primary dithizonates. The secondary cobalt dithizonate had partly decomposed. There was no reason to doubt the identities of the remaining compounds.

Using the spectra of col. 13, yields were calculated for those dithizonates, for which molar absorptivities in chloroform were available. The yields were for Ni 96 %, Hg 102 %, Tl 90 %, Zn 99 % and for Cd 90 %. However, high yields were not regarded essential, because the bromide disk method in its present form is only semi-quantitative.

Infrared spectra. The infrared records were made using a pure KBr disk in the reference beam. The latter was diaphragmed, so that the part with the lowest absorption came to lie near the 0 % absorption line. The positions of the peaks were corrected by calibrating the instrument each day with the help of a Beckman polystyrene film. The blanks (from alkaline solutions) rarely gave noticeable peaks. Instrument noise occurred mainly in the 1900–1300 cm^{-1} region. It was located in records of blanks and pure KBr disks and taken into account, when the sample spectra were evaluated. The heights of the peaks were measured from base-lines, often including a group of peaks. Special base-lines had to be drawn for small peaks in the neighborhood of larger ones. An approximation of the true intensity of each peak was sought.

The peak intensities were recalculated from % absorption to absorbance (A) and absorptivities were calculated as 100 A/d, where d is the dithizonate content of a disk expressed in micro-equivalents. The approximate absorptivities thus obtained, from the three disks in each experiment, were found to be roughly constant.

RESULTS

Peak wave-numbers and intensities of the infrared spectra are collected in Tables 2 and 3. Comparisons showed, that the spectra could be arranged in four distinct groups:

1. Dithizone.
2. Primary dithizonates of nickel(II), palladium(II), platinum(II) and cobalt.
3. Secondary copper(II) dithizonate.
4. Primary dithizonates of gold(III), silver(I), mercury(II), thallium(I), copper(II), zinc(II), cadmium(II), indium(III), lead (II) and bismuth(III).

The results indicate, that the two groups of primary dithizonates may have different structures. The nickel, palladium, and platinum dithizonate spectra within group 2 were closely related and also those of copper, zinc, indium and lead dithizonate in group 4. Some of them seemed difficult to tell apart, but on closer inspection differences became apparent. Further discussion and an attempt to interpret the spectra will be published later.

REFERENCES

1. Harding, M. M. *J. Chem. Soc.* **1958** 4136.
2. Irving, H. and Cox, J. J. *J. Chem. Soc.* **1961** 1470.
3. Duncan, J. F. and Thomas, F. G. *J. Chem. Soc.* **1960** 2814.
4. Iwantscheff, G. *Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse*, Verlag Chemie, Weinheim 1958.
5. Dyfverman, A. *Anal. Chim. Acta* **21** (1959) 357.

Received March 11, 1963.