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Compounds Containing a Monovalent Metal Cation, an Organic Anion, and an α,α'-Dioximino Cyclic Ketone[1]

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A new and unusual class of compounds containing a monovalent metal ion, an organic anion, and a 2,6-dioximinocyclohexanone in a 1:1:1 mole ratio has been discovered. Sodium, potassium, and silver cations gave compounds of this type; rubidium gave compounds containing also two moles of water. Only aromatic sulfonate anions participated in compound formation with the alkali metal cations, whereas with silver cation, aromatic sulfonate, phenylphosphonate, and trifluoroacetate anions all gave compounds. 2,5-Dioximinocyclopentanone formed compounds with aromatic sulfonate anions and silver cation, but not with alkali metal cations. These compounds contained 2,5-dioximinocyclopentanone, anion, cation, and water in a 1:1:1:1 mole ratio. All the compounds of 2,6-dioximinocyclohexanones appeared to exist only in the solid state and to be completely dissociated in solution.

Introduction

In the early stages of a recent study[2] aimed at the synthesis of the amino acid lysine, a deficiency of benzenesulfonyl chloride was used to induce a single Beckmann rearrangement of 2,6-dioximinocyclohexanone to 5-cyano-2-oximinovaleric acid. Since a solution of the disodium salt of 2,6-dioximinocyclohexanone was used, the final reaction mixture contained, in addition to the sodium salt of the desired acid, the disodium salt of 2,6-dioximinocyclohexanone and sodium benzenesulfonate. When this mixture was acidified, the expected precipitation of excess 2,6-dioximinocyclohexanone did not occur, but instead a solid was obtained which, after recrystallization from water–ethanol, gave an analysis which indicated that it contained 2,6-dioximinocyclohexanone, sodium ion, and benzenesulfonate ion in a 1:1:1 mole ratio.

The present investigation was undertaken to learn if the formation of compounds of this type was a general phenomenon, and, if so, to determine what the properties and structures of the compounds were.

Experimental[3]

The decomposition points are uncorrected. Infrared spectra were taken on Nujol mulls with a Perkin-Elmer Model 137 Infracord recording spectrophotometer. The molecular weight determinations by vapor pressure osmometry were performed on a Mechrolab Model 301 vapor pressure osmometer, using water as solvent. Ebulliometric molecular weight measurements were made in water or methanol as solvents.

General Procedure for the Preparation of Alkali Metal Coordination Compounds.—To a solution of 75 mmoles of the alkali metal hydroxide in 25 ml. of water was added 25 mmoles of the α,α'-dioximino ketone. A red-orange solution resulted. To this was added 25 mmoles of the sulfonic acid dissolved in 25 ml. of water (more if necessary). There was no evidence of change. Cautious addition, with cooling, of enough 5 *N* hydrochloric acid to make the solution strongly acid brought down a light brown solid. The red color gradually lightened and disappeared by the time the mixture was just strongly acid. Frequently the slurry of solid was so thick that additional water had to be added to get a filterable mixture. The solid was recovered by suction filtration and dried *in vacuo*. Sodium-containing compounds were recrystallized from water–ethanol; potassium- and rubidium-containing compounds from water alone.

General Procedure for the Preparation of Silver Coordination Compounds.—To a solution of 4.2 g. (75 mmoles) of potassium hydroxide in 25 ml. of water was added 25 mmoles of the α,α'-dioximino ketone. To the resulting red-orange solution was added 25 mmoles of the sulfonic or other acid dissolved in 25 ml. of water (more if necessary). The resulting solution was poured slowly into a solution of 4.2 g. (25 mmoles) of silver nitrate and 10 ml. of 5 *N* nitric acid in 25 ml. of water. A yellow solid precipitated immediately and was collected by suction filtration and dried *in vacuo*. The silver compounds containing 2,6-dioximinocyclohexanone required very large amounts of water for recrystallization, about 700 ml./g. The compounds containing 2,5-dioximinocyclopentanone were much more soluble and were recrystallized from water–ethanol.

Results and Discussion

The results of all experiments performed are presented in Table I. In summary, it was found that when solutions containing the disodium salt of 2,6-dioximinocyclohexanone or 2,6-dioximino-4-methylcyclohexanone[4] and any of a variety of aromatic sodium sulfonates in 0.2–0.5 *M* concentration each were made strongly acid, solids precipitated which contained sodium ion, sulfonate ion, and the 2,6-dioximinocyclohexanone in a 1:1:1 mole ratio. Sulfonate anions which gave such substances were benzenesulfonate, *p*-toluenesulfonate, 2-naphthalenesulfonate, sulfanilate, 5-nitro-*o*-toluenesulfonate, and 2,5-dichlorobenzenesulfonate. When a number of other anions were tried, only 2,6-dioximinocyclohexanone was recovered on acidification. These anions included 1,3-benzenedisulfonate, 2,6-naphthalenedisulfonate, 1,3,5-naphthalenetrisulfonate, *d*-10-camphorsulfonate, methanesulfonate, trichloroacetate, benzoate, and phenylphosphonate. Similar substances containing potassium ion were obtained also, but from only two relatively water-insoluble anions, 2-naphthalenesulfonate and 2,5-dichlorobenzenesulfonate. The same two anions were

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[1] Presented in part at the Fifteenth Annual Kansas City Chemistry Conference, Nov. 15, 1963.

[2] A. F. Ferris, G. S. Johnson, F. E. Gould, and H. K. Latourette, *J. Org. Chem.*, **25**, 492 (1960).

[3] Microanalyses and molecular weight determinations by ebullition were performed by Galbraith Laboratories, Knoxville, Tenn.

[4] A. F. Ferris, F. E. Gould, G. S. Johnson, and H. Stange, *J. Org. Chem.*, **26**, 2602 (1961).

TABLE I

COORDINATION COMPOUNDS CONTAINING A MONOVALENT METAL CATION, AN ANION, AND AN α,α'-DIOXIMINO KETONE

Anion	Metal ion	Dioximino cyclic ketone	Empirical formula	Yield, %	Dec. pt., °C.	Mol. wt.			C, %		H, %		N, %		S, %		Metal, %	
						Calcd.[a]	Ebull.	V.p.o.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Benzenesulfonic	Na	2,6	$C_{12}H_{13}O_6N_2SNa$	74	300	113	100	112	42.85	43.14	3.90	3.88	8.33	8.34	9.53	9.34	6.84	6.73
p-Toluenesulfonic	Na	2,6	$C_{13}H_{15}O_6N_2SNa$	71	300	117	143	128	44.57	44.43	4.32	4.44	8.00	8.00	9.15	9.07	6.56	6.48
2-Naphthalenesulfonic	Na	2,6	$C_{16}H_{15}O_6N_2SNa$	86	285	129	151	137	49.74	49.47	3.91	3.92	7.28	7.43	8.30	8.54	5.95	5.69
Sulfanilic	Na	2,6	$C_{12}H_{14}O_6N_3SNa$	91	285	117	129	108	41.02	40.84	4.02	4.12	11.96	11.75	9.13	8.93	6.54	6.49
5-Nitro-*o*-toluenesulfonic	Na	2,6	$C_{13}H_{14}O_8N_3SNa$	71	295	132	151	130	39.49	39.65	3.57	3.64	10.63	10.55	8.11	8.21	5.82	5.92
2,5-Dichlorobenzenesulfonic	Na	2,6	$C_{12}H_{11}O_6N_2SCl_2Na$	58	295	134	150	144	35.60	35.83	2.74	2.97	6.91	7.12	7.91	7.77	5.67	5.81[b]
p-Toluenesulfonic	Na	4-CH_3-2,6	$C_{14}H_{17}O_6N_2SNa$	91	230	121	135		46.15	45.81	4.70	4.68	7.68	7.39	8.80	8.58	6.30	6.63
2-Naphthalenesulfonic	Na	4-CH_3-2,6	$C_{17}H_{17}O_6N_2SNa$	77	230				51.00	50.79	4.28	4.21	7.00	7.21	8.00	7.83	5.74	6.01
p-Toluenesulfonic	Ag	2,6	$C_{13}H_{15}O_6N_2SAg$	91	240				35.87	35.79	3.47	3.55	6.44	6.30	7.37	7.32	24.79	24.51
2-Naphthalenesulfonic	Ag	2,6	$C_{16}H_{15}O_6N_2SAg$	85	250				40.78	40.54	3.21	3.22	5.94	5.74	6.80	7.01	22.89	22.88
2,5-Dichlorobenzenesulfonic	Ag	2,6	$C_{12}H_{11}O_6N_2SCl_2Ag$	100	265				29.41	29.25	2.26	2.09	5.72	5.61	6.54	6.67	22.01	21.80[c]
Trifluoroacetic	Ag	2,6	$C_8H_8O_5N_2F_3Ag$	98	195				25.48	25.61	2.14	2.26	7.43	7.49			28.61	28.63[d]
Phenylphosphonic	Ag	2,6	$C_{12}H_{15}O_6N_2PAg$	95	205				34.14	33.95	3.58	3.72	6.64	6.79			25.56	25.63[e]
2-Naphthalenesulfonic	K	2,6	$C_{16}H_{15}O_6N_2SK$	50	200	134	147		47.74	47.62	3.76	3.88	6.96	6.84	7.97	7.96	9.71	9.64
2,5-Dichlorobenzenesulfonic	K	2,6	$C_{12}H_{11}O_6N_2SCl_2K$	55	230	141	165		34.21	34.05	2.63	2.74	6.65	6.58	7.61	7.38	9.28	9.11[f]
2-Naphthalenesulfonic	Rb[g]	2,6	$C_{16}H_{19}O_8N_2SRb$	66	220	162	165		39.63	40.00	3.94	3.96	5.77	6.02	6.61	6.60	17.63	17.26
2,5-Dichlorobenzenesulfonic	Rb[g]	2,6	$C_{12}H_{15}O_8N_2SCl_2Rb$	55	245	168	180		28.61	28.62	3.00	3.04	5.56	5.40	6.36	6.21	16.97	17.17[h]
p-Toluenesulfonic	Ag[i]	2,5	$C_{12}H_{15}O_7N_3SAg$	59	210				32.81	32.82	3.44	3.36	6.38	6.13	7.30	7.12	24.56	24.71
2,5-Dichlorobenzenesulfonic	Ag[i]	2,5	$C_{11}H_{11}O_7N_2SCl_2Ag$	90	220	247[j]	248		26.74	26.62	2.24	2.31	5.67	5.58	6.49	6.65	21.83	21.57[k]
5-Nitro-*o*-toluenesulfonic	Ag[i]	2,5	$C_{12}H_{14}O_9N_3SAg$	92	210				29.77	29.50	2.91	2.59	8.68	8.49	6.62	6.59	22.28	22.50

[a] Calcd. for dissociation into three fragments. [b] Calcd.: Cl, 17.50. Found: Cl, 17.34. [c] Calcd.: Cl, 14.47. Found: Cl, 14.51. [d] Calcd.: F, 15.12. Found: F, 14.90. [e] Calcd.: P, 7.34. Found: P, 7.50. [f] Calcd.: Cl, 16.83. Found: Cl, 16.63. [g] Compounds contain two molecules of water. [h] Calcd.: Cl, 14.08. Found: Cl, 14.29. [i] Compounds contain one molecule of water. [j] Calcd. for dissociation into two fragments. [k] Calcd.: Cl, 14.35. Found: Cl, 14.36.

the only ones which gave rubidium-containing compounds. The rubidium compounds differed from the others in also containing two moles of water. No substances of this type were obtained from lithium ion or ammonium ion and any anion.

The silver counterparts of the alkali metal compounds had to be made by an indirect route, because there was no way of putting the 2,6-dioximinocyclohexanone into solution as a silver salt. The expedient used was to put the dioximino ketone and the sulfonate into solution as the potassium salts, and then add this solution to a solution containing silver nitrate and excess nitric acid. Under these conditions, compounds containing silver ion, an anion, and 2,6-dioximinocyclohexanone in a 1:1:1 mole ratio were obtained as very insoluble yellow solids from the following anions: *p*-toluenesulfonate, 2-naphthalenesulfonate, 2,5-dichlorobenzenesulfonate, trifluoroacetate, and phenylphosphonate.

When 2,5-dioximinocyclopentanone[4] was used as the dioximino ketone the only alkali metal compound obtained was that from sodium naphthalenesulfonate. This material, however, was so unstable that it decomposed when recrystallization was attempted. On the other hand, silver-containing compounds were formed with 2,5-dioximinocyclopentanone from *p*-toluenesulfonate, 2,5-dichlorobenzenesulfonate, and 5-nitro-*o*-toluenesulfonate anions. These compounds were different from their 2,6-dioximinocyclohexanone counterparts, since they contained silver ion, sulfonate anion, 2,5-dioximinocyclopentanone, and *water* in a 1:1:1:1 mole ratio.

In the formation of all these compounds, it appeared that the solubility factor was of paramount importance. When acid was added to a solution containing a monovalent cation, an anion, and a dioximino ketone, the least soluble species, either dioximino ketone or 1:1:1 compound, began to precipitate and continued to do so as more acid was added and equilibria were shifted in the direction of the precipitating species. In a few cases analysis of crude samples showed that some dioximino ketone was coprecipitating with 1:1:1 compound, but the amount was sufficiently small to be eliminated by recrystallization. In general, the silver compounds were very insoluble in water, the sodium compounds somewhat soluble in hot water or water-methanol, and the potassium and rubidium compounds considerably more soluble in these solvents.

Molecular weight determinations on the 2,6-dioximinocyclohexanone compounds in water (and, in a few cases, in methanol) by both ebulliometry and vapor pressure osmometry were very consistent and indicated that all compounds of this type were essentially completely dissociated in solution into metal ion, anion, and dioximino ketone. The silver compounds of 2,6-dioximinocyclohexanone were too insoluble for molecular weight determinations, but infrared evidence (see below) makes it appear that chemically they are the same as the alkali metal materials. It thus appears that the 2,6-dioximinocyclohexanone compounds exist only in the solid state. This does not appear to be true of the 2,5-dioximinocyclopentanone silver compounds, since the only one of these soluble enough for molecular weight determination was dissociated into only two fragments in solution.

Unlike the dioximino ketones, which decompose in a few weeks at room temperature, the 1:1:1 compounds are stable indefinitely. Samples of the compound formed from sodium benzenesulfonate and 2,6-dioximinocyclohexanone have been kept as long as 3 years with no evidence of change. When heated, the compounds did not melt but decomposed vigorously at reasonably characteristic temperatures. The compounds differed in appearance depending on the nature of the metal cation. The sodium compounds, when highly purified, were white and fibrous, resembling masses of absorbent cotton. The potassium and rubidium compounds were tan and flaky, and the silver compounds yellow and flaky.

The infrared spectra of all these compounds contained most of the prominent bands associated with both organic components. Bands at 1700, 1580, 1095, and 895 cm.$^{-1}$, characteristic of 2,6-dioximinocyclohexanone, were prominent at the same or very nearly the same wave lengths in the spectra of all the compounds containing it. Similarly, bands at 1190, 1040, 1014, and 815 cm.$^{-1}$, characteristic of the *p*-toluenesulfonate anion, were present in the spectra of all materials containing it. The characteristic bands of other sulfonate anions also appeared in the spectra of compounds derived from them. For any particular combination of dioximino ketone and anion the spectra were practically independent of the nature of the cation. Thus, for the combination of 2,6-dioximinocyclohexanone and the 2-naphthalenesulfonate anion, the sodium, potassium, rubidium, and silver compounds gave practically superimposable spectra.

Assignment of a structure to the unusual compounds derived from the 2,6-dioximinocyclohexanones presents an intriguing problem which cannot be solved completely on the basis of data presented in this paper. The very exact stoichiometry exhibited by the new compounds implies some sort of chemical bonding between the metal cation and the 2,6-dioximinocyclohexanone. Since the only valence band available to the metal cation is satisfied by the sulfonate anion, the cation must be bound to the 2,6-dioximinocyclohexanone by coordinate bonds. The normal requirement of the alkali metal cation for at least tetracovalence requires three coordinate bonds to the dioximino ketone, but study of molecular models suggests that bonding of any of the monovalent cations to the three functions of a single dioximino ketone is virtually impossible. The metal ion therefore must bridge two dioximino ketone molecules and be coordinated to a ketone and an oxime function in one molecule and to an oxime function in a second molecule. Either a dimeric or a polymeric structure can fulfill this requirement, and there is no way on the basis of present data to choose between them. In any case, the larger size of the rubidium cation permits it to assume a covalency of six and add two molecules of water.

The infrared spectra of the 2,5-dioximinocyclopentanone compounds differ considerably from those of the 2,6-dioximinocyclohexanone compounds containing the same anion. This, together with the molecular weight data and the presence of a single molecule of water in the compounds, indicates that the structure of the 2,5-compounds is probably completely different from that of the 2,6- compounds. The 2,5- compounds are probably analogous to the known[5–7] coordination compounds of simple α-oximino ketones and contain coordinate bonds to the ketone, one oxime group, and water, and a valence bond to the sulfonate anion. Solution would then involve simply separation of the anion, resulting in the two fragments found.

These structural suggestions admittedly are tentative, and complete elucidation of the structures of these compounds must lie with X-ray diffraction studies. It is apparent, however, that the 2-6-dioximinocyclohexanone compounds represent an unusual class of materials, since they are almost certainly coordination compounds, yet they are not "complexes" in the classic sense because they exist only in the solid state.

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Circular Dichroism of Coordination Compounds. IV. Some Metal Complexes with Dithiooxalic Acid[1]

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The circular dichroism (CD) and absorption data for the visible and ultraviolet regions are reported for the complex ions $[Co(C_2S_2O_2)_3]^{3-}$, $[Rh(C_2S_2O_2)_3]^{3-}$, and $[Cr(C_2S_2O_2)_3]^{3-}$, along with the preparation and absorption data of $[Co(en)_2(C_2S_2O_2)]Cl \cdot 2H_2O$. The CD data made it possible to relate the assignments of transitions for the tris(dithiooxalato) complexes and to assign their absolute configurations.

Introduction

There have been many papers[2] concerned with the absorption spectra of complexes formed by ligands containing sulfur, but few have dealt with complexes of dithiooxalate[3] and the interpretation of their spectra. The interpretation of the spectra of the dithiooxalate complexes has been made difficult by the presence of broad, intense bands in the visible region which overlap the intense near-ultraviolet absorption bands of the ligand itself. In an earlier paper in this series[4] it was demonstrated that circular dichroism (CD) data are very useful for locating the individual components in such situations. The present study is concerned with visible and near-ultraviolet absorption and CD spectra of $(+)_{546}$-$[Co(C_2S_2O_2)_3]^{3-}$, $(+)_{546}$-$[Cr(C_2S_2O_2)_3]^{3-}$, and $(+)_{546}$-$[Rh(C_2S_2O_2)_3]^{3-}$ and the absorption spectrum of the new compound $[Co(en)_2(C_2S_2O_2)]Cl$.

Experimental

Measurements.—Absorption measurements were made at room temperature using a Cary Model 14 spectrophotometer for 2×10^{-5}–2×10^{-2} *M* solutions in 1-cm. cells. Optical rotations were obtained with a Rudolph Model 80Q6 polarimeter at room temperature and CD spectra were recorded with a Roussel–Jouan dichrograph at 4–5°, maintained by circulating ice water through the cell compartment. Measurements of CD (2, 1, 0.2, and 0.1 cm. cells) and optical rotation (5 cm. cell) were made using 2×10^{-4}–1×10^{-3} *M* solutions. In the CD measurements, the slit widths were always kept under 0.1 cm.

Preparation of Bis(ethylenediamine)dithiooxalatecobalt(III) Chloride Dihydrate, $[Co(en)_2(C_2S_2O_2)]Cl \cdot 2H_2O$.—Potassium dithiooxalate (3.5 g.) was added to a solution (35 ml.) of *cis*-$[Co(en)_2Cl_2]Cl$ (5.4 g.) and the mixture was warmed at about 60° on a water bath. The color of the solution changed from violet to dark brown. After about 10 min. a reddish brown crystalline powder began to separate along with some black material. The mixture was filtered and the precipitate discarded. The filtrate was kept for a few hours in an ice bath and filtered to remove a crop of reddish brown crystals which were separated by filtration. The crude product was recrystallized from a small volume of hot water and washed with 50% ethanol and then with absolute ethanol. The fine crystals obtained were dried in a vacuum desiccator over H_2SO_4. *Anal.* Calcd. for $[Co(N_4C_4H_{16})(C_2S_2O_2)]Cl$: C, 12.53, H, 4.82; N, 16.74; S, 19.16. Found: C, 12.97; H, 5.08; N, 17.06; S, 19.43. The optical resolution of this complex using silver α-bromo-*d*-camphor-π-sulfonate and silver antimonyl-*d*-tartrate as resolving agents was attempted without success.

Other Preparations and Resolutions. The compounds $(+)_{546}$-$KBa[Co(C_2S_2O_2)_3] \cdot 5H_2O$, $(+)_{546}$-$KBa[Rh(C_2S_2O_2)_3] \cdot 6H_2O$, and $KCa[Cr(C_2S_2O_2)_3] \cdot 6H_2O$ were prepared and resolved using $(-)_{546}$-*cis*-$[Co(en)_2(NO_2)_2]Cl$ as the resolving agent following the directions of Dwyer and Sargeson.[5] The observed specific rotations (546 mμ) of the Co and Rh complexes were: +500° (lit.[5]

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