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THE PREPARATION OF SOME TROPONE COMPLEXES

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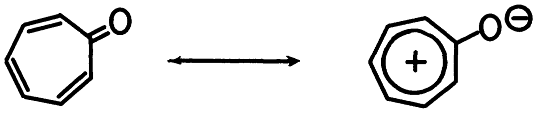
Tropone and its various derivatives were found to form several complexes having a composition of 1 : 1, 1 : 2, or 2 : 1 with mercury (II), zinc (II), cadmium (II), copper (II), cobalt (II), manganese (II), and nickel (II). In all cases, co-ordination would occur with the carbonyl oxygen.

Tropolones have been known to give salts or chelate complexes with various metals, the properties of which can be applied to the purification of tropolones and to the analyses of metals.1) On the other hand, tropone has a high dipole moment (4.30)2) and a strong basicity (pKa -1.02)3) indicating the charge distribution is closely represented by the following resonance form, although the molecular orbital calculation,4) nmr study,5) and X-ray crystallographic analysis6) indicate that the bond alternation is considerably large on the ground state of tropone in contrast to tropolone in which the bond alternation could not be observed.



Tropone formed stable salts such as hydroxytropylium chloride and picrate,1) although the structure of the latter has not been clarified yet. Furthermore, the fact that 2-methoxytropone formed crystalline water complex1) suggested, by comparison with well known N-oxides, phosphine oxides, sulfoxides and cyclopropenone derivative,7) that tropone would prefer to co-ordinate through oxygen with metals. Recently, the formation and the X-ray crystallography of π-complex of tropone or tropylium ions with various metal carbonyls have been reported.8)

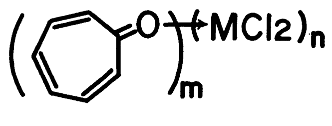
Tropone and its various derivatives including 2-substituted tropones, benzotropones, tropolone, thiotropone9) and N-phenyltroponeimine9) were found to form easily complexes with chlorides of various metals. Table 1 shows compositions determined by elemental analyses, color, melting points, and infrared absorption bands of the complexes obtained. Most of the complexes were recrystallized from appropriate solvents including water, alcohol, chloroform, and benzene.

Tropone formed 1 : 1 or 1 : 2 complexes with $HgCl_2$ having fairly low melting points, 2 : 1 complexes with $ZnCl_2$, and 1 : 1 complexes with $CdCl_2$, $CoCl_2$, $MnCl_2$, or $NiCl_2$ having high melting points. Tropone also formed 1 : 1 complex containing one mole of water with $CuCl_2$ as golden yellow needles, and the water was easily liberated upon heating *in vacuo* to give water free brown crystals.

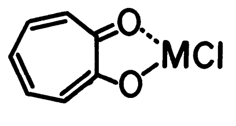
Tropolone and hinokitiol afforded 1 : 1 complexes with $HgCl_2$ or $CdCl_2$ similar to tropones, and ir spectra of the complexes show νOH bands at around 3220 cm^{-1}. When tropolone and anhydrous $CuCl_2$ were mixed in methanol, pale brown crystals having a composition of $C_7H_5O_2CuCl$ corresponding to [1 : 1 complex - HCl] precipitated. When the crystals were added in water, color changes to green and give a known chelate complex $(C_7H_5O_2)_2Cu$.$^{1)}$ Tropolone also gave the similar complex with $ZnCl_2$.

Tropones are easily liberated from the complexes by hydrolysis, chromatography on silicic acid, or by treatment with dioxane; for instance, $HgCl_2$ complexes liberate tropones by dissolving in dioxane by ligand exchange to form dioxane-$HgCl_2$ complex. All complexes are very stable in air at room temperature in contrast to ligands themselves, therefore, the complex formations are very useful for separation and storage of tropones, and tropones may become useful reagents for reversible trapping of metals.

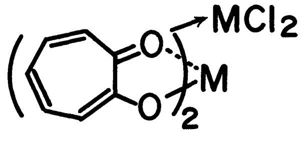
In order to clarify the structure of these complexes, ir, uv and nmr spectra were measured. The uv and nmr spectra are similar to those of the ligands. However, it was found that ir spectra are considerably different. The large shifts (5~50 cm^{-1}) of νC=O, νC=C, and νC=S to the lower frequencies are observed in all tropone-metal complexes compared to those of ligands.$^{10)}$ The phenomenon can be explained by the co-ordination which would occur through the carbonyl oxygen (or thiocarbonyl sulfur in case of thiotropone) with metals forming σ-complexes in all cases as shown by the structure (A).$^{11)}$ We can devise two structures (B) and (C) for the complexes of tropolone with $CuCl_2$ or $ZnCl_2$. Infrared spectra of the complexes are similar each other, and different from those of tropone-metal complexes and of tropolone copper chelate complex especially between 1400~1200 cm^{-1} region. Therefore, it is assumed that the structure (B) is more plausible in view of the pale brown color of the complex obtained here.



(A)



(B)



(C)

TABLE 1. Compositions and Some Properties of Complexes

Complexes*	Color	mp (°C)	IR Bands** 10)
Tpn $HgCl_2$	white needles	119-120	1628(m),1547(s)
2-Cl-Tpn $HgCl_2$	white plates	174-175	1618(m),1570(s),1538(s)
2-Br-Tpn $HgCl_2$	white plates	164-165	1618(m), 1569(s)
2-AcO-Tpn $HgCl_2$	white plates	111-112	1625(w),1600(w),1553(s)
2-BzO-Tpn $HgCl_2$	white needles	156-164	1592(m),1550(m),1504(m)
2-MeO-Tpn $(HgCl_2)_2$	white needles	199-200	1611(m),1588(m),1528(s),1510(s)
2-MeS-Tpn $(HgCl_2)_2$	pale yellow prisms	135-136	1610(m),1571(w),1529(s)
2-Me_2N-Tpn $(HgCl_2)_2$	brown prisms	105(d)	1610(m),1538(m),1510(s)
2,3-BenzoTpn $HgCl_2$	white needles	178-180	1630(w),1548(s)
4,5-BenzoTpn $HgCl_2$	white needles	189-190	1620(s),1563(s)
Tropolone $(HgCl_2)_{3/2}$	white needles	154-155	3230(m),1612(m),1601(m),1532(m)
Hinokitiol $HgCl_2$	white needles	104-106	3210(m),1609(s),1530(m),1468(s)
$(Tpn)_2$ $ZnCl_2$	white plates	171-172	1626(m),1590(w),1500(s)
$(2\text{-}MeS\text{-}Tpn)_2$ $ZnCl_2$	yellow cryst.	218-220	1601(m),1500(s)
$(2\text{-}Me_2N\text{-}Tpn)_2$ $ZnCl_2$	yellow prisms	183-183.4	1591(m),1508(s),1492(s)
Tpn $CdCl_2$	white plates	>300	1628(m),1534(s)
2-MeO-Tpn $CdCl_2$	pale yellow prisms	>300	1615(w),1594(m),1520(s)
2-MeS-Tpn $CdCl_2$	pale yellow needles	>300	1605(m),1525(s)
2-Me_2N-Tpn $CdCl_2$	yellow needles	>300	1590(m),1570(m),1513(s)
Tropolone $CdCl_2$	white needles	>300	3225(m),1600(s),1553(m),1475(s)
Tpn $CuCl_2$ H_2O	golden yellow needles	207-208	1626(m),1515(s)
Tpn $CuCl_2$	brown cryst.	207-208	1626(m),1515(s)
2-MeO-Tpn $CuCl_2$	brown cryst.	284-285(d)	1612(w),1590(m),1513(s)
Tpn $CoCl_2$	pale violet needles	>300	1626(m),1530(s),1514(m)
Tpn $MnCl_2$	yellow needles	>300	1627(m),1532(s),1514(m)
2-MeO-Tpn $MnCl_2$	orange prisms	>300	1615(w),1590(m),1520(s)
Tpn $NiCl_2$	yellow cryst.	>300	1628(m),1532(s),1515(m)
Tropolone $CuCl_2$ - HCl	pale brown cryst.	275-277	1596(m),1576(m),1513(s)
Tropolone $ZnCl_2$ - HCl	yellow cryst.	>300	1595(m),1576(w),1512(s)
Thiotropone $HgCl_2$	yellow cryst.	145(d)	1040(s)***
Thiotropone $CdCl_2$	orange cryst.	140(d)	1070(s)***
N-Ph-Troponeimine $HgCl_2$	yellow cryst.	101(d)	1630(m),1531(s),1500(s)****
N-Ph-Troponeimine $CdCl_2$	yellow cryst.	230(d)	1631(m),1535(s),1509(s)****

* Tpn = tropone, Hinokitiol = 4-isopropyltropolone

** Measured in KBr disk (cm^{-1}), and only characteristic bands are listed.

*** Absorption band of C=S of thiotropone appears at 1080(s) cm^{-1}.9)

**** Absorption bands of N-phenyltroponeimine appear at 1636(m), 1550(m), 1556(s) cm^{-1}.9)

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10) Infrared spectra of troponoids are discussed by Y. Ikegami, Kagaku no Ryoiki, Extra Vol. 38, 1959, pp 33-84; *Bull. Chem. Soc. Japan*, **35**, 967, 972 (1961); νC=C and νC=O bands appear around 1640~1610 (m) and 1595~1565 (s) cm^{-1}, respectively, by coupling of energy levels, private communication from Dr. Ikegami.

11) The X-ray crystallographic analysis of 2-methoxytropone-$CdCl_2$ complex was accomplished, the result of which will be reported elsewhere.

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