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Six-coordinate Chromium(III) Complexes with *N,N'*-Ethylene-bis(acetylacetoneiminate) as a Ligand[1]

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Numerous six-coordinate chromium(III) complexes with *N,N'*-ethylene-bis(acetylacetoneiminate) (abbreviated as Acen) have been synthesized. The complexes obtained are of the type $[Cr(Acen)X_2]Y$, where $X=H_2O$, NH_3, CH_3NH_2, $n\text{-}C_3H_7NH_2$, and $n\text{-}C_4H_9NH_2$ for $Y=Cl$ and $X=CN$, NCS, and NO_2 for $Y=K$. The complex $[Cr(Acen)(H_2O)_2]Cl$ has been obtained by a reaction of anhydrous chromium(III) chloride with *N,N'*-ethylene-bis(acetylacetoneimine) in tetrahydrofuran. The other complexes have been derived from the diaquo-complex. Infrared spectra show that the nitrite ions in $[Cr(NO_2)_2(Acen)]^-$ and the thiocyanate ions in $[Cr(NCS)_2(Acen)]^-$ are bound with the chromium(III) ion through oxygen and nitrogen atoms, respectively. Electronic absorption bands of all these complexes, which arise from internal transitions within the ligand Acen, differ greatly from those of the free ligand, suggesting that the electronic states of the ligand in the complexes differ from those of the free ligand.

A number of papers have been published on metal complexes with Schiff bases.[2,3] However, not many chromium(III) complexes have so far been reported.[4-7] Chromium(III) complexes with Schiff bases obtained from salicylaldehyde derivatives and various amines have recently been synthesized.[4,5] As an extension of the previous study on six-coordinate chromium(III) complexes with *N,N'*-ethylenebis(salicylideneiminate) (abbreviated as Salen),[6] this paper deals with six-coordinate chromium(III) complexes with *N,N'*-ethylenebis(acetylacetoneiminate)[8] as a quadridentate ligand (I, abbreviated as Acen). These complexes have not been reported, although tris(*N*-arylacetylacetoneiminato)chromium(III) complexes have been known for some years.[7]

Experimental

Materials. Chromium(III) complexes with *N,N'*-ethylene-bis(acetylacetoneiminate) as a ligand are shown in Table 1, together with analytical data.

$[Cr(Acen)(H_2O)_2]Cl$. *N,N'*-ethylene-bis(acetylacetoneimine) (0.1 mol) and potassium ethoxide (0.2 mol) in ethanol

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[1] Presented at the 21st Symposium on Coordination Chemistry, Nagoya, October, 1971.

[2] R. H. Holm, G. W. Everett, Jr., and Chakravorty, "Progress in Inorganic Chemistry," Vol. VII, ed. by F. A. Cotton, Interscience, New York (1966), p. 83.

[3] S. Yamada, *Coordin. Chem. Rev.*, **1**, 415 (1966).

[4] M. J. O'Connor and B. O. West, *Austral. J. Chem.*, **21**, 369 (1968).

[5] S. Yamada and K. Iwasaki, This Bulletin, **41**, 1972 (1968).

[6] S. Yamada and K. Iwasaki, *Inorg. Chim. Acta*, **5**, 3 (1971); This Bulletin, **42**, 1463 (1969).

[7] J. P. Collman and E. T. Kittleman, *Inorg. Chem.*, **1**, 499 (1962).

[8] For the sake of convenience, this ligand is referred to as *N,N'*-ethylene-bis(acetylacetoneiminate) in the present paper.

Table 1. Analytical data of complexes of the type $[Cr(Acen)X_2]Y \cdot nH_2O$

X	Y	*n*	found, % C	found, % H	found, % N	calcd, % C	calcd, % H	calcd, % N
H_2O	Cl	1	41.68	6.20	8.02	41.30	6.41	8.10
NH_3	Cl	1.5	38.90	7.24	15.24	38.86	7.34	15.11
CH_3NH_2	Cl	2	40.09	7.71	13.89	41.22	7.90	13.74
$C_2H_5NH_2$	Cl	1.5	45.04	8.33	13.09	45.01	8.26	13.12
n-$C_3H_7NH_2$	Cl	1	48.87	8.60	12.74	48.47	8.59	12.56
n-$C_4H_9NH_2$	Cl	1	50.17	8.99	11.99	50.67	8.93	11.82
$C_6H_5NH_2$	Cl	2.5	52.95	6.62	10.58	53.28	6.89	10.36
CN	K	2	42.07	5.57	14.45	41.88	5.52	13.96
NO_2	K	0	35.75	4.45	13.91	35.55	4.47	13.82
NCS	K	1	37.35	4.50	12.60	37.57	4.50	12.52

(50 ml) were added to 300 ml of tetrahydrofuran in a flask attached to a Soxhlet apparatus. Anhydrous chromium(III) chloride (0.1 mol) and zinc dust (1 g) were placed in the thimble of the apparatus, and the tetrahydrofuran solution was allowed to reflux for about 4 hr until the recycling liquid became colorless. The reaction mixture was allowed to cool down to room temperature. Potassium chloride which precipitated in the solution was filtered, and a reddish brown filtrate obtained was concentrated nearly to dryness on a rotary evaporator. The residue was dissolved again in ethanol (150 ml), and the resulting solution was filtered, diluted with 200 ml of benzene and concentrated to about 50 ml. The procedure with the residue was repeated several times. Brown crystals which separated out in the solution were collected by filtration and dried *in vacuo* for 24 hr.

$[Cr(Acen)(NH_3)_2]Cl \cdot 1.5H_2O$. $[Cr(Acen)(H_2O)_2]Cl$ (0.01 mol) was dissolved in a mixture of methanol (50 ml) and 30% aqueous ammonia (50 ml) at about 50°C. The resulting solution was heated at this temperature for 15 min, filtered and allowed to stand overnight. Reddish orange needle-like crystals which separated out in the solution were collected.

$[Cr(Acen)(RNH_2)_2]Cl \cdot nH_2O$. ($R=CH_3$, C_2H_5, n-C_3H_7, and n-C_4H_9; n=2, 1.5, 1, and 1, respectively). $[Cr(Acen)(H_2O)_2]Cl$ (0.01 mol) was added to a solution of an appropriate alkyl amine (0.2—0.3 mol) in methanol (20—30 ml) and the solution was stirred for 15 min at about 50°C. Diethyl ether or benzene was added to the solution until the solution became turbid. It was then allowed to stand overnight to give orange needle-like crystals.

$[Cr(Acen)(C_6H_5NH_2)_2]Cl \cdot 2H_2O$. Aniline (0.1 mol) and $[Cr(Acen)(H_2O)_2]Cl$ (0.01 mol) were added to acetone (50 ml), stirred at about 50°C for 15 min, then filtered and allowed to stand overnight. Yellow-brown crystals were collected.

$K[Cr(CN)_2(Acen)] \cdot 2H_2O$. An aqueous solution of potassium cyanide (0.04 mol) was added to a solution of $[Cr(Acen)(H_2O)_2]Cl$ (0.01 mol) in methanol (30 ml). The resulting solution was heated at about 50°C for 15 min and allowed to stand overnight to give reddish orange crystals.

The chromium(III) complexes described so far were pure enough without recrystallization. However, purification was carried out whenever necessary by recrystallization from methanol or ethanol. The complexes are soluble in methanol, ethanol, water, tetrahydrofuran and acetonitrile, but insoluble in diethyl ether and benzene.

$K[Cr(NCS)_2(Acen)] \cdot H_2O$. A suspension of $[Cr(Acen)(H_2O)_2]Cl$ (0.01 mol) and potassium thiocyanate (0.04 mol) in acetone (50 ml) was heated at about 50°C for 1 hr. The potassium chloride which separated out in the solution was removed by filtration. The filtrate was concentrated to yield the crude product of the desired complex which was recrystallized from acetone. Dark red crystals were obtained. The compound is soluble in acetone.

$K[Cr(ONO)_2(Acen)]$. A suspension of $[Cr(Acen)(H_2O)_2]Cl$ (0.01 mol) and potassium nitrite (0.045 mol) in methanol (50 ml) was heated under stirring at about 50°C for 1 hr, and the resulting potassium chloride was filtered. On concentrating the filtrate, the desired complex was obtained as yellowish brown crystals. Purification was carried out by filtration from methanol or ethanol.

All the complexes except for the dicyano-complex are gradually decomposed by water. The diisothiocyanato-complex undergoes decomposition even in methanol or ethanol.

Measurements. The electronic absorption spectra of the chromium(III) complexes were determined with a Shimadzu MPS-50L spectrophotometer. The infrared absorption spectra were measured in the region 600—4000 cm^{-1} with a Hitachi EPI-G31 infrared spectrophotometer using Nujol mull and potassium bromide disc methods.

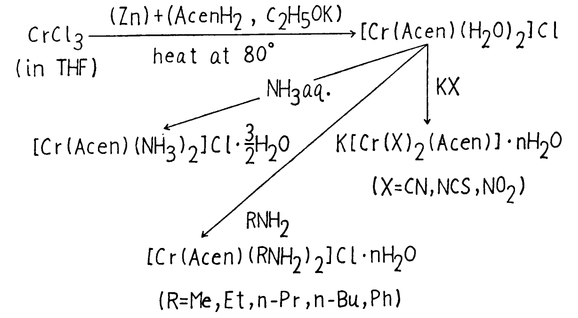
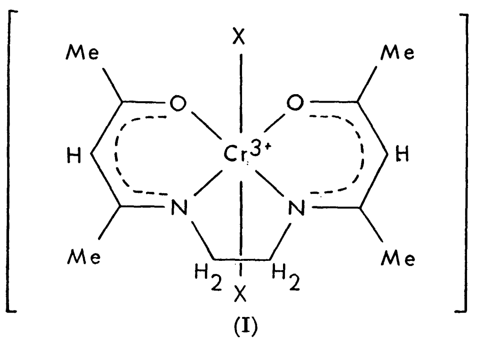


Fig. 1. Synthetic routes of the complexed of the type $[Cr(Acen)X_2]Y$

Results and Discussion

The synthetic routes of the chromium(III) complexes are summarized in Fig. 1. A method which involves reactions in ethyleneglycol at a higher temperature and which was successful for preparing $[Cr(Salen)(H_2O)_2]Cl$,[5,6] did not yield $[Cr(Acen)(H_2O)_2]Cl$, but gave instead tris(acetylacetoneiminato)chromium(III). The method for preparing $[Cr(Acen)(H_2O)_2]Cl$ proved to be more appropriate for the synthesis of $[Cr(Salen)(H_2O)_2]Cl$ than the previously one.

Since the quadridentate ligand Acen usually requires, but not necessarily a square-planar coordination, it most likely that the chromium(III) complexes prepared have a six-coordinate, *trans*-configuration.



(I)

The main infrared bands of $[Cr(ONO)_2(Acen)]^-$ and $[Cr(NCS)_2(Acen)]^-$ are shown in Table 2. From the table and with the aid of the criteria previously established,[9,10] it is concluded that the nitrite ions in $[Cr(ONO)_2(Acen)]^-$ are coordinated through their oxygen atoms to the chromium(III) ion. This is in agreement with the results for other chromium(III) complexes.[11]

Table 2. Infrared absorption maxima of thiocyanato-isothiocyanato and nitro-nitrito isomers

Nitro-nitrito isomers	ν_{as}	ν_s	δ	reference
free NO_2^- (in $NaNO_2$)	1328	1261	828	a
$K[Cr(ONO)_2(Acen)]$	1450	1075	847	this work
		1063	835	
$[Cr(ONO)(NH_3)_5]Cl_2$	1460	1048	839	b
$[Co(ONO)(NH_3)_5]Cl_2$	1468	1065	825	b
$[Co(NO)_2(NH_3)_5]Cl_2$	1428	1310	824	b
thiocyanato-isothiocyanato isomers	ν(CN)	ν(CS)		
free NCS^- (in KNCS)	2053	748		c
$K[Cr(NCS)_2(Acen)]\cdot H_2O$	2085	785		this work
$NH_4[Cr(NCS)_4(NH_3)_2]$	2120	823		c
$[Co(NCS)(NH_3)_5](ClO_4)_2$	2125	806		d
$[Co(SCN)(NH_3)_5](ClO_4)_2$	2100	710		d
$(Et_4N)_2[Pd(SCN)_4]$	2109	694		e
	2112	698		

ν : cm^{-1}

(a) R.E. Weston and T.F. Broodasky, *J. Chem. Phys.*, **27**, 683 (1957).
(b) K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, **80**, 4817 (1958).
(c) J. Lewis, R.S. Nyholm, and P.W. Smith, *J. Chem. Soc.*, **1961**, 4590.
(d) D.A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 635 (1970).
(e) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959(1965).

In a similar way, we see that the thiocyanate ions are bound through their nitrogen atoms to the chromium(III) in $[Cr(NCS)_2(Acen)]^-$. It seems to be generally accepted that the ν (CS), which appears at about 690 to 860 cm^{-1}, is useful for the diagnostic purposes, the band being observed at 780 to 860 cm^{-1} for the M–NCS complex and at 690 to 730 cm^{-1} for the M–SCN complex.

The electronic absorption spectra of some of the chromium(III) complexes are shown in Fig. 2, the maxima of the bands being given in Table 3. It should be noted that, as far as the main peaks are concerned, the absorption spectra of the complexes are similar, regardless of the position of a ligand X in the spectrochemical series. As an example, the maxima of these bands for $[Cr(CN)_2(Acen)]^-$ are nearly the same as those for $[Cr(Acen)(H_2O)_2]^+$, in spite of the fact that the cyanide ion is far apart from H_2O in the spectrochemical series. Consequently, it is concluded that the bands at about 22—23, 27—28, and 36—37 kK observed for all the chromium(III) complexes may not be assigned to *d-d* bands. It is more likely that they correspond to internal transitions within the coordinated Acen and/or transitions, in which the ligand Acen is mainly involved. This situation seems to be similar to that with complexes of the type $[Cr(Salen)L_2]$.[6]

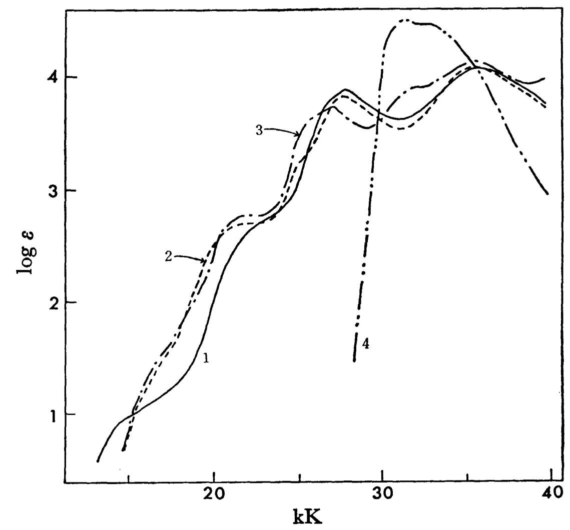


Fig. 2. Electronic absorption spectra of complexes of the type $[Cr(Acen)X_2]Y$ in solution: 1, X=H_2O, in methanol: 2, X=CN, in methanol; 3, X=NCS, in acetonitrile; 4, *N,N'*-ethylene-bis(acetylacetoneimine), in methanol

Their ligand field bands are probably hidden under more intense bands of other origins, except for some complexes which show a small shoulder in the lower frequency side of the absorption curves, possibly arising from *d-d* transitions.

The inflation at about 32 kK in the spectrum of $[Cr(NCS)_2(Acen)]^-$ indicates the presence of a band, which may be assigned to a "specific absorption band" due to the isothiocyanate group linked with the chromium(III) ion. A band of a similar nature has also been reported to appear in the neighbourhood of this frequency region for chromium(III) ammine complexes.[12] A specific absorption band due to the coordinated nitrite ion is known to be generally weaker and may be considered to be hidden under more

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[9] J. L. Burmeister, *Coordin. Chem. Rev.*, **3**, 225 (1968).

[10] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **4**, 721 (1965); A. Takeuchi, K. Sato, K. Sone, S. Yamada, and K. Yamasaki, *Inorg. Chim. Acta*, **1**, 399 (1967).

[11] W. W. Fee, C. S. Garmer, and J. N. M. Harrowfield, *Inorg. Chem.*, **6**, 87 (1967).

[12] R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 471 (1938).

Table 3. Main absorption maxima of complexes of the type $[Cr(Acen)X_2]Y$ in solution[a]

X	ν (logε)[b]			
H_2O	15.7 (1.05),	23.0 (2.68),	27.7 (3.88),	36.1 (4.08)
NH_3	22.6 (2.59),	27.7 (3.80),	36.2 (4.06)	
CH_3NH_2	22.5 (2.68),	27.5 (3.78),	36.2 (4.08)	
n-$C_3H_7NH_2$	22.6 (2.58),	27.5 (3.78),	36.2 (4.05)	
$C_6H_5NH_2$	22.8 (2.68),	27.8 (3.84),	35.9 (4.12)	
CN	22.0 (2.68),	27.8 (3.84),	36.0 (4.06)	
NCS[c]	22.0 (2.78),	27.0 (3.74),	32.0 (3.90),	36.0 (4.14)
NO_2[d]	16.3 (1.24),	22.6 (2.60),	27.7 (3.83),	36.2 (4.04)
free ligand $AcenH_2$	31.0 (4.48),	33.0 (4.45)		

a) Unless otherwise indicated, the values in the table refer to those of the methanolic solutions.
b) ν: 10^3 cm^{-1}
c) in acetonitrile
d) in methanol containing sodium nitrite

intense bands of other origins.

We see from Fig. 2 and Table 3 that the bands of $[Cr(Acen)X_2]$, due to internal transitions within the ligands, differ remarkably from those of the free ligand itself. This is also found to be the case with the corresponding cobalt(III) complexes,[13] which show spectra with main features similar to those of the chromium(III) complexes. This indicates that the electronic state of the ligand in the chromium(III) complexes, as well as in the cobalt(III) complexes, differ from that in the free ligand. Comparison also shows that the spectra of tris(N-arylacetylacetoneiminato)chromium(III) complexes[7] have features similar to those of complexes of the type $[Cr(Acen)X_2]Y$.

Since it is known that these free ligands exist in the form of β-ketoamines rather than β-ketoimines,[14] the above result seems to show that their electronic state in the chromium(III) complexes differs considerably from that of the β-ketoamines.

The present authors are grateful to the Ministry of Education for financial support.

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[13] G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organometal. Chem.*, **6**, 181 (1966).

[14] G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 2099 (1966).