

carboxylate groups. A band at $\sim 1730\text{ cm}^{-1}$ which has been assigned to $\nu\text{C}=\text{O}$ in metal carboxylates^{6,7}, where carboxylic acid behaves as a unidentate ligand, was found to be present in all these derivatives. Two other bands present at ~ 1560 and $\sim 1450\text{ cm}^{-1}$ may be assigned to $\nu_a\text{COO}^-$ and $\nu_s\text{COO}^-$ respectively. These indicate the bidentate⁸ nature of carboxylate groups.

No bands are observed in the regions ~ 3500 , ~ 1130 and $1100\text{--}900\text{ cm}^{-1}$ corresponding to hydroxy, isopropoxy and $\text{Ti}=\text{O}$ stretching⁹⁻¹¹ respectively, indicating the absence of any free acid or $\text{Ti}(\text{OPr}^i)_2(\text{OOCR})_2$ species. However, a broad band around 835 cm^{-1} observed in these derivatives may be assigned to $\text{Ti}=\text{O} \rightarrow \text{Ti}$ type of linkage¹². As the molecular weight data are not in agreement with polymeric or dimeric structures, it may be suggested that the coordination between terminal oxygen and titanium atoms is destroyed in solution giving rise to monomeric species and consequently the molecular weight falls corresponding to the molecular complexity 1:3.

These derivatives have no tendency of adduct formation with nitrogen containing ligands like pyridine.

The compounds are thermally stable up to 200° above which temperature these decompose slowly, giving CO , CO_2 , H_2O and leaving TiO_2 as the residue. About 80% of its decomposition is completed around 300° .

This mode of decomposition of $\text{TiO}(\text{OOCR})_2$ derivatives is different from that of other metal carboxylates^{13,14} in which the decomposition proceeds with the formation of a ketone as an intermediate product.

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References

1. DEHNICKE, K., *Chem. Ber.*, **98** (1965), 291.
2. COLLIS, R. E., *J. chem. Soc. (A)*, (1969), 1895.
3. SELBIN, J., *J. chem. Educ.*, **41** (1964), 87.
4. HARWOOD, J. H., *Industrial applications of organo-metallic compounds* (Chapman & Hall, London), 1962.
5. PANDEY, K. C. & MEHROTRA, R. C., *J. prakt. Chem.*, **5** (1967), 101.
6. PIKE, R. M. & LUONGO, R. R., *J. Am. chem. Soc.*, **87** (1965), 1403.
7. PIKE, R. M. & LUONGO, R. R., *J. Am. chem. Soc.*, **88** (1966), 2972.
8. STEPHENSON, T. A., MOREHOUSE, S. M., POWELL, A. R., HEFFER, J. P. & WILKINSON, G., *J. chem. Soc. (A)*, (1965), 3632.
9. COX, M., LEWIS, J. & NYHOLM, R. S., *J. chem. Soc.*, (1965), 2840.
10. FOWLES, G. W. A., LEWIS, D. F. & WALTON, R. A., *J. chem. Soc. (A)*, (1968), 1468.
11. BARRACLOUGH, C. G., LEWIS, J. & NYHOLM, R. S., *J. chem. Soc.*, (1959), 3552.
12. KALINNIKOV, V. T., ZELENTSOV, V. V., VOLKOV, M. N. & SHOSTAKOVSKII, S. M., *Chem. Abstr.*, **62** (1965), 9941 C.
13. MISRA, S. N., MISRA, T. N. & MEHROTRA, R. C., *J. inorg. nucl. Chem.*, **25** (1963), 195.
14. RAI, A. K. & MEHROTRA, R. C., *J. Indian chem. Soc.*, **40** (1963), 359.

Pentacoordinated Ti(IV) Chloride & Sn(IV) Bromide & Iodide Complexes with Acridine & Piperazine

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Donor-acceptor type complexes of TiCl_4 , SnBr_4 and SnI_4 with acridine and piperazine have been prepared and characterized on the basis of conductance and IR data. A pentacoordinated trigonal bipyramidal structure has been proposed for all the complexes. The $(\text{TiCl}_4)_2$ -piperazine complex has been found to be binuclear.

IN continuation of our earlier work^{1,2} on the complexes of acridine and piperazine with SnCl_4 and GeCl_4 , the preparation and characterization of TiCl_4 , SnBr_4 and SnI_4 complexes with these donor molecules are reported in this note. The possibility of the formation of a binuclear complex with piperazine has also been considered. Molecular addition compounds of group (IV) halides have extensively been studied³⁻⁸.

Acridine (Fluka AG, m.p. 108°) was recrystallized from alcohol. Piperazine hexahydrate (E. Merck, m.p. 56°) was used as such without further purification. Anhydrous Ti(IV) chloride (BDH) was used whereas Sn(IV) bromide and iodide were prepared according to standard methods⁹.

Acridine complexes—A solution of Sn(IV) bromide/iodide in ethanol-chloroform mixture was added to an ethanolic solution of acridine in approximately equimolar quantity. Sn(IV) bromide yielded a greenish yellow crystalline substance but Sn(IV) iodide gave a gelatinous mass which dissolved on stirring. However, this solution later yielded a yellowish orange compound. Ethanolic solutions of Ti(IV) chloride and excess of acridine when left overnight after mixing yielded needle-shaped crystals. All the solids obtained were washed with ethanol and dried *in vacuo*.

Piperazine complexes—These were also prepared as above but the complex formation was rapid in the case of Sn(IV) iodide and Ti(IV) chloride whereas with Sn(IV) bromide a granular product was obtained after a few minutes.

The melting points and analyses of the complexes are given in Table 1. All the addition compounds formed with acridine and piperazine are of the type $\text{MX}_4 \cdot \text{L}$, except the adduct of TiCl_4 with piperazine which is of $(\text{MX}_4)_2 \cdot \text{L}$ type.

The molar conductances (Systronix conductivity bridge) of approximately 10^{-3} millimolar solutions of the adducts of acridine in nitromethane at room temperature fall well below the range for a univalent electrolyte¹⁰, indicative of non-ionic nature of these adducts.

Acridine exhibits two strong bands in its IR spectrum at 1515 and 1555 cm^{-1} attributable to $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$ respectively. Its adducts with TiCl_4 , SnBr_4 and SnI_4 exhibit $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$

TABLE 1 — ADDUCTS OF ACRIDINE AND PIPERAZINE

Adduct	m.p. °C	Found (%) (Calc.)	
		N	X
TiCl ₄ -Acr	235	4.06 (3.80)	38.62 (38.91)
SnBr ₄ -Acr	246*	2.41 (2.26)	51.20 (51.71)
SnI ₄ -Acr	177	2.10 (1.73)	63.62 (63.20)
(TiCl ₄) ₂ Ppr	300*	5.99 (6.20)	30.03 (30.40)
SnBr ₄ -Ppr	283*	5.41 (5.34)	62.01 (61.60)
SnI ₄ -Ppr	350*	4.21 (3.90)	71.68 (71.30)

Acr = acridine; Ppr = piperazine

*Melted with decomposition.

3. ROLSTEN, R. F. & SISLER, H. H., *J. Am. chem. Soc.*, **79** (1957), 1068.
4. SISLER, H. H., BATEY, H. H., PFAHLER, B. & MATTAIR, R., *J. Am. chem. Soc.*, **70** (1948), 3021.
5. SISLER, H. H., SHILLING, E. E. & GROVES, W. O., *J. Am. chem. Soc.*, **73** (1951), 426.
6. AGGARWAL, R. C. & SINGH, P. P., *J. inorg. nucl. Chem.* **28** (1966), 1651.
7. AGGARWAL, R. C. & SINGH, P. P., *J. inorg. nucl. Chem.* **28** (1966), 1655.
8. BEATTIE, I. R., *Q. Rev. chem. Soc.*, **17** (1963), 382.
9. *Handbook of preparative inorganic chemistry*, edited by G. Brauer (Academic Press, New York), 1963, 729.
10. GEARY, W. J., *Coord. chem. Rev.*, **7** (1971), 1130.
11. GREENWOOD, N. N. & WADE, K., *J. chem. Soc.*, (1960), 1130.
12. OKISHI, Y., IMAI, Y. & AIDA, K., *J. inorg. nucl. Chem.* **35** (1973), 101.

Complexes of Re(IV) with 2-Hydroxy- & 8-Hydroxy-quinolines & o-Phenanthroline

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2-hydroxy- and 8-hydroxy-quinolines and o-phenanthroline initially form compounds of the types H₂ [hydroxyquinoline]₂ReCl₆ and H₂ [(o-phen)₂ReCl₆] respectively with potassium hexachlororhenate(IV). On reaction with excess ligands, these compounds are converted into the corresponding hydroxo complexes of the types Re(OH)Cl(oxyquinoline)₂ and Re(OH)Cl₂-(o-phen). The compounds are paramagnetic with $\mu_{\text{eff}} = 2.1\text{--}3.78$ BM indicating a quadrivalent state for Re in these compounds.

IN continuation of our earlier work¹⁻³ on Re(IV and V) complexes of pyridine and picolines, further work on the complexes of Re(IV) with hydroxy-quinolines and o-phenanthroline is reported in this note.

Re(IV) complexes with hydroxyquinolines — Two types of compounds were formed with 2- and 8-hydroxyquinolines. H₂[(2-hydroxyquinoline)₂-ReCl₆] and H₂[(8-hydroxyquinoline)₂-ReCl₆] were obtained as yellow crystalline solids on mixing an aqueous solution of hexachlororhenate⁴ (1 g) with the respective hydroxyquinolines (1.5 g) dissolved in dilute acetic acid. The solid obtained in each case was filtered, washed and dried over fused CaCl₂. The compounds are almost resistant towards dilute acids but turn black on treatment with alkali.

The hydroxochloro-bis(oxyquinoline) Re(IV) complexes, [Re(OH)Cl(2-oxyquinoline)₂] and [Re(OH)Cl(8-oxyquinoline)₂], were formed when the respective yellow hydroxyquinoline salts were warmed with excess of the respective hydroxyquinolines in acetic acid (0.1M) on a water-bath. The precipitate separated in each case was filtered, washed and dried *in vacuo*.

The compounds are insoluble in water or ethanol but completely dissolve in boiling nitrobenzene. The compounds did not suffer any loss in weight on heating to 130°. These are non-conducting in nitrobenzene.

at 1590, 1625; 1575, 1630; and 1575, 1640 respectively. It is known that coordination through the nitrogen atom of the pyridyl group¹¹ causes an increase in the C=N stretch. It is noteworthy that this shift in the Sn(IV) halide adducts increase with increasing halogen size and is smallest for Ti(IV) chloride adducts. All the complexes are thus suggested to have a trigonal bipyramidal geometry. However, the possibility of a hexa-coordinated structure with halide bridging could not be ruled out.

In the far IR spectrum the acridine complexes of TiCl₄ show two strong bands at 410 and 460 cm⁻¹ and a weak band at 375 cm⁻¹ which may be due to Ti-N and Ti-Cl bands.

Molar conductances of piperazine adducts could not be measured owing to their insolubility in organic solvents.

A comparison of IR spectra of piperazine and its complexes shows appreciable negative shift in the $\nu\text{N-H}$; from 3328 cm⁻¹ in the ligand to 3150, 3000 and 3080 and 3300 cm⁻¹ in adducts with TiCl₄, SnBr₄ and SnI₄ respectively. An increase in the C=N stretching frequency from 1444 cm⁻¹ in the free ligand to 1460, 1480 and 1450 cm⁻¹ in the adducts with TiCl₄, SnBr₄ and SnI₄ respectively is also observed. The decrease in the $\nu\text{N-H}$ is attributed to coordination of Sn(IV) or Ti(IV) with the nitrogen atom of piperazine. The 1:2 complex of TiCl₄ with piperazine¹² may assume a five-coordinated binuclear structure by coordinating with two TiCl₄ molecules through the nitrogen atoms of a piperazine molecule. Two distinct bands at 378 and 365 cm⁻¹ in the far IR region have been observed and assigned to Ti-Cl bond.

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References

1. ZAIDI, S. A. A. & SIDDIQI, K. S., *Z. anorg. allg. Chem.*, **379** (1970), 329.
2. ZAIDI, S. A. A. & SIDDIQI, K. S., *J. inorg. nucl. Chem.*, **35** (1973), 655.