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Adduct Formation of Tris(morpholine-4-carbo-dithio- or diselenoato)-Co(III) Complexes with Iodine

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Spectrophotometric studies of dichloromethane solutions of iodine with tris(morpholine-4-carbo-dithio- or diseleno-ato)Co(III) complexes (respectively Co(modtc)$_3$ and Co(modsc)$_3$ and collectively CoL$_3$) have shown the existence of a CoL$_3$·I$_2$ adduct. The thermodynamic and spectral characteristics of these complexes have been determined. On this basis the adduct is regarded as a C.T. complex of the S or Se (collectively = X) donor sites of CoL$_3$ molecule towards iodine. The stability constants found are in the order K(Co(modsc)$_3$·I$_2$) ≫ K(Co(modtc)$_3$·I$_2$), according to the general trend of stability constants related to Se and S derivative adducts with iodine.

By addition of benzene to the CH$_2$Cl$_2$ solutions of the adducts, lustrous dark-brown crystals formulated as CoL$_3$·2I$_2$ are obtained.

Introduction

The reactions of iodine with metal N,N-dialkyl-dithiocarbamato complexes have been widely studied, and can give rise to: i) metal oxidation as in the reaction of gold(I), copper(II) and nickel(II) derivatives [1]; ii) ligand oxidation as in the zinc(II), cadmium(II) and mercury(II) dithiocarbamates [2]; iii) several types of products as in the dithiocarbamato iron(III) reactions [3].

On the other hand, organic sulphur and better still, selenium derivatives, having in particular thio- or seleno-carbonyl groups, easily form molecular complexes with iodine [4a, b, c]. Coordinative equilibria may be mechanistic precursors in substitutive and oxidative reactions [5a, b]. Therefore an investigation of the characteristics of adduct formation seemed very interesting.

This paper reports a study of adduct formation between iodine and tris(morpholine-4-carbo-dithio- or diseleno-ato)Co(III) in CH$_2$Cl$_2$ solution and in the solid state, and provides a critical evaluation of the formation constants.

Experimental

Materials and Instruments

Co(modtc)$_3$ and Co(modsc)$_3$ complexes were prepared according to the literature [6, 7].

Doubly sublimed iodine was purchased from Carlo Erba. Methylene chloride was Merck reagent grade and kept over 4 Å molecular sieves.

CoL$_3$·2I$_2$ were obtained by benzene addition to a CH$_2$Cl$_2$ solution of CoL$_3$ and an excess of iodine. *Anal.* Calcd for Co(modsc)$_3$·2I$_2$; C, 13.50; H, 1.81; N, 3.14; Co, 4.42; I, 38.03. Found C, 13.4; H, 1.7; N, 3.1; Co, 4.3; I, 38.9. Calcd for Co(modtc)$_3$·2I$_2$: I, 48.19 and for Co(modsc)$_3$·I$_2$: I, 31.75. Found: I, 45.7 (the compound slowly loses iodine).

The u.v.–vis. spectra were recorded on a Cary mod. 219 Spectrophotometer equipped with a Lauda K2RD thermostat (±0.1 °C) using 1.00 cm matched quartz cells.

The i.r. spectra were obtained with a Perkin-Elmer mod. 325 Spectrophotometer in KBr pellets, CH$_2$Cl$_2$ solutions or nujol mulls.

C, H, N analyses were performed by the Istituto di Chimica Farmaceutica, University of Cagliari, and the iodine was determined with a combustion method followed by a spectrophotometric determination of the sublimed iodine.

Calculations

The association constants of the reaction under investigation were calculated, assuming a 1:1 interaction, from the absorbance values of nine solutions using a BASIC program based on a modified Conrow method [8]. The absorbances were monitored at 10, 15, 20, 25 and 30 °C. The solutions were made up at 20 °C and the concentrations at the other temperatures were corrected for the volume variation of the solvent. The concentrations of the solutions were 2.5 × 10^{-5} M in Co(modsc)$_3$ and ranged from 7.5 × 10^{-6} to 2 × 10^{-4} M in I$_2$. In the Co(modtc)$_3$ case they were respectively 2.10 × 10^{-4}

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TABLE I. Stability Constants, ϵ Values and Thermodynamic Parameters of the Adduct Formation between $Co(modsc)_3$ and I_2 in CH_2Cl_2 Solutions.

T (°C)	λ (nm)	K^a ($l\,mol^{-1}$)	ϵ^a ($l\,mol^{-1}\,cm^{-1}$)	$\bar{K} \pm \sigma\bar{K}$ ($l\,mol^{-1}$)
30	350	190.300	34.420	$(18.7 \pm 0.6) \times 10^4$
	360	187.600	35.770	
	370	186.500	34.080	
	380	187.200	30.200	
25		199.500	34.400	$(19.7 \pm 0.6) \times 10^4$
		195.200	35.790	
		198.600	34.010	
		195.400	30.040	
20		207.400	34.790	$(20.4 \pm 0.6) \times 10^4$
		204.100	36.020	
		206.600	33.920	
		201.400	30.280	
15		205.300	34.760	$(20.8 \pm 0.6) \times 10^4$
		207.800	36.390	
		209.700	34.390	
		210.700	30.670	
10		219.700	34.910	$(22.0 \pm 0.6) \times 10^4$
		219.000	36.700	
		221.100	34.440	
		220.500	30.440	

$\Delta H° = (1.3 \pm 0.1)$ kcal mol^{-1}; $\Delta S° = (19.9 \pm 0.4)$ e.u. (error limits from linear regression).

[a] Standard deviations are for all K values about ±16,000 and for $\epsilon \pm 170$; values are reported with the same number of digits even if they are not all significant.

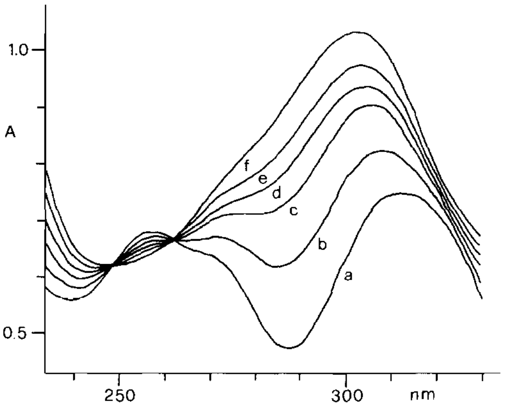

Fig. 1. Ultraviolet absorption spectra: a = $[Co(modsc)_3] = 2.31 \times 10^{-5}$ *M*, b, c, d, e and f with addition of stoichiometric amounts of iodine in the ratio 1:1, 1:2, 1:3, 1:4, 1:5 respectively.

M and 2.5×10^{-4}–2.0×10^{-2} *M*, and in a second run the complex concentration ranged from 2×10^{-4} to 2×10^{-3} *M*, and the iodine concentration was 2×10^{-4} *M*.

Results and Discussion

The addition of iodine in CH_2Cl_2 to CoL_3 in the same solvent is accompanied by a drastic change in the UV–Visible spectra of these solutions. In the $Co(modsc)_3$ case there is a new clear C.T. maximum at 295 nm and a blue shift (λ^* = 450 nm) of the visible iodine band. Moreover, a blue shift of the peak characteristic of the free complex is observed [9]. Two isosbestic points are clearly visible at 239 and 265 nm, showing an equilibrium between two absorbing species only (Fig. 1).

In the $Co(modtc)_3$ case it is possible to observe a modification of the spectrum only in the visible region, because there is evidence of the adduct formation only with high concentrations of the reagents. The blue shifted iodine band appears as a shoulder and cannot be resolved due to overlapping with the strong bands of the adduct and the complex. On

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*This wavenumber (see Fig. 2) was obtained by means of a curve decomposition program in order to correct it for overlap with the other bands.

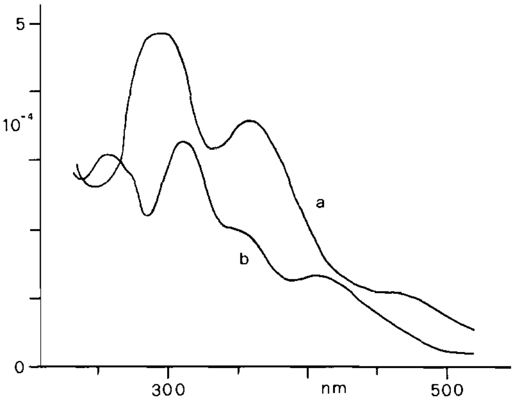

Fig. 2. UV–vis absorption spectra of: a) the Co(modsc)$_3$·I$_2$ adduct calculated as an average of six experimental spectra by using the formation constant at 25 °C; b) the Co(modsc)$_3$ complex.

adding iodine to the complex this overlapping produces a continuous increase of the absorbance but not the isosbestic points.

The stoichiometry of these adducts was determined using the continuous variation method [10]. There is clearly observed the formation of 1:1 adducts and no other stoichiometry in solution. The stability constants were calculated applying Conrow's method [8]. After a rough preliminary estimation of the Ks, the concentrations of the solutions were chosen according to the criterion discussed elsewhere [8] to obtain reliable K values in the limits of our experimental constraints.

In Table I the thermodynamic characteristics of the Co(modsc)$_3$·I$_2$ adduct in dichloromethane are reported. We point out that in the Co(modsc)$_3$·I$_2$ case, also in our best experimental conditions, the K values are affected by a 10% error, while the ϵ values are determined with an error lower than 1%. This finding is due (see discussion in ref. [8]) to the fact that since the adduct is almost completely associated, the saturation fraction is near one and therefore ϵ is carefully determined, while the K values are affected by a large error. The calculated spectrum of the Co(modsc)$_3$·I$_2$ adduct is reported in Fig. 2.

As far as the Co(modtc)$_3$ case is concerned, the measurements run using an excess of iodine (2.5 X 10^{-4}–2 X 10^{-2} *M*) give K = (2.5 ± 0.4) X 10^2 l mol^{-1} and ϵ = (1.500 ± 40) l mol^{-1} cm^{-1} at 25 °C. However these measurements are affected by a temperature dependence of the free iodine absorbance (probably due to some I$_4$ formation) making the evaluation of the thermodynamic parameters meaningless. The symmetrical measurements using constant iodine concentrations and a variable excess of the complex give K = (6 ± 2) X 10 l mol^{-1} and ϵ = (6 ± 2) X 10^3 l mol^{-1} cm^{-1} at 25 °C and λ = 580 nm.

No appreciable dependence of the K (Co(modtc)$_3$ case) on temperature was observed, suggesting a $\Delta H°$ value near to zero. However the K values are determined with 30% error limits, because with our instrument we were not able to use cells with higher pathlengths for the more dilute solutions, in order to reduce the relative experimental error.

These 1:1 adducts were not obtained in the solid state, because the crystalline, lustrous dark-brown solids obtained from the CoL$_3$ + I$_2$ solutions by precipitation with benzene are always formulated as CoL$_3$·2I$_2$, in accordance with their analytical results.

In the i.r. spectra of the CoL$_3$·2I$_2$ adducts in the solid state three regions are different from those of the parent CoL$_3$ compounds [7, 11] namely:

i) the band near 1480 cm^{-1}, primarily associated with the thio- or seleno-ureide absorption, is shifted to higher wavenumbers and split on passing from the parent CoL$_3$ to the iodine adduct (the $\bar{\nu}$ values obtained are: X = S: 1500sh, 1490s; X = Se: 1510m, 1490s cm^{-1}, KBr pellets).

ii) also ν(C=X) absorptions are split each into two bands (X = S: $\bar{\nu}$ = 1000mw and 983m cm^{-1}; X = Se: $\bar{\nu}$ = 863mw and 838m).

iii) the region characteristic of the ν(Co–X) vibration is affected by iodine addition (X = S: $\bar{\nu}$ = 365m, 350w; X = Se: $\bar{\nu}$ = 304m and 267m, nujol mulls).

Similar features are maintained in the spectra of the CH$_2$Cl$_2$ solutions of CoL$_3$ + I$_2$ in the region around 1480 cm^{-1}, but especially in the less associated Co(modtc)$_3$·I$_2$ case, they were obtained in excess of iodine.

These facts suggest that the resonance from $R_2\overset{+}{N}$= CX_2^{-2} makes a greater contribution to the total structure of the ligand in the adduct case, and that some differentiation exists between the three ligands, or even between the two X atoms of the same chelating group.

Since u.v.–vis and i.r. spectra of the isolated CoL$_3$·2I$_2$ compounds in CH$_2$Cl$_2$ solution are equivalent to those of CoL$_3$·I$_2$, and since in solution there is no evidence for formation of other adducts except those in the 1:1 ratio, we suggest that the second iodine molecule present in the solid adduct should interact not with the CoL$_3$ core but with the first coordinated iodine.

The formation constant related to the Se derivative adduct is much higher than that of the sulphur one, other factors being equal. Such a large difference, and the spectroscopic results, point out that the interaction mainly involves X atoms.

The electron donation of X atoms when contained in organic derivatives towards iodine is well documented [4] and our results point out that these atoms, even if contained in coordinated dithio- or diseleno-carbamates, retain basic properties.

The $\Delta H°$ value obtained for the Co(modsc)$_3$·I$_2$ adduct, lower than uncoordinated seleno-carbonyl derivatives [12], is in accordance with the lowered basicity of the Se atom as a consequence of the ligand coordination.

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