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Notes

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Carbonyl Hemochromes[1]

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Received August 12, 1975 AIC50605Y

Many hemoproteins combine with carbon monoxide to form well-defined and quite stable carbonyl complexes, which have characteristic electronic, infrared, and Mossbauer spectra.[2] For these reasons, the carbonyl is one of the most frequently prepared hemoprotein derivatives. All carbonyl hemes contain diamagnetic iron(II).

Few simple (nonprotein) iron porphyrin carbonyls (carbonyl hemochromes, containing six-coordinated iron(II)) have been systematically studied, except for the work by Caughey et al.[3,4] on the CO infrared stretching frequencies of several carbonyl hemochromes. A recent report by Collman et al.[5] describes some carbonyls of a "picket fence" heme.

We have prepared several carbonyl hemochromes and have measured their infrared and Mössbauer spectra. The results are reported here.

Experimental Section

The bis(morpholine), bis(pyrrolidine), and bis(piperidine) hemochromes of *meso*-tetra(*p*-anisidyl)porphinatoiron(II) (PMXPPFe·2L, L = morph, pyrr, pip) were prepared by reaction of the hemin chloride [PMXPPFeCl] with the neat hot amine, and the bis(pyridine) and bis(imidazole) hemochromes (L = py, Im) by displacement of piperidine from the bis(piperidine) hemochrome.[6] In all cases, except for imidazole, the hemochrome was recrystallized several times from the hot amine in order to remove any amine hydrochloride and all traces of the only slightly soluble μ-oxo contaminant, $(PMXPPFe)_2O$. The bis(imidazole) hemochrome was washed well with ether to remove excess imidazole.

For the preparation of the carbonylamine-*meso*-tetra(*p*-anisidyl)porphinatoiron(II) complexes, about 0.5 g of the bis(amine) hemochrome was added to about 50 ml of methylene chloride or benzene, saturated with carbon monoxide. (It is important to prevent the bis(amine) hemochrome in solution from coming into contact with oxygen as it is easily oxidized to the unreactive μ-oxo compound.) After 10–15 min of stirring under carbon monoxide, the solution was filtered, and, while bubbling carbon monoxide through the filtrate, it was reduced to about 10 ml by heating. Addition of pentane caused the formation of crystals, which were collected, washed with pentane, and dried at room temperature. Yields were nearly quantitative.

Table I. Mössbauer and Infrared Data of Carbonyl Hemochromes at 298 K

Compd	ν_{CO},[a] cm^{-1}	δ,[b] mm/s	Δ,[c] mm/s	Γ,[d] mm/s	N[e]
PMXPPFe·morph·CO	1996	+0.49	0.55	0.36	0.90
PMXPPFe·pip·CO	1981	+0.47	0.49	0.30	1.64
PMXPPFe·py·CO	1978	+0.46	0.49	0.29	1.38
PMXPPFe·pyrr·CO	1982	+0.45	0.45	0.29	1.35
PMXPPFe·Im·CO	1966	+0.45	0.36	0.29	0.98

[a] Average value of carbonyl stretching frequency determined for KBr pellet and Halocarbon oil mull samples; ±5 cm^{-1}. [b] Isomer shift relative to sodium nitroprusside; ±0.03 mm/s. [c] Quadrupole splitting; ±0.03 mm/s. [d] Line width at half-maximum. [e] Number of γ-ray counts under nonresonant conditions; $\times 10^6$.

Infrared spectra were obtained on a Beckman IR-8 spectrophotometer with samples prepared in Halocarbon oil mulls and KBr pellets. Differences in CO stretching frequencies were less than 5 cm^{-1} for the two samples and only average values are reported.

Mössbauer spectra were obtained with a scanned-velocity spectrometer operating in the time mode and calibrated with sodium nitroprusside and ^{57}Fe foil. Spectra were fitted with a least-squares approximation assuming two Lorentzian line shapes of equal width. Estimated error limits on the isomer shift, δ, and quadrupole splitting, Δ, are ±0.03 mm/s. A Calcomp plotter was used to plot data.

Results and Discussion

The CO stretching frequency occurred as a single, sharp, strong peak in the 1965–1996-cm^{-1} range for the five carbonylaminetetraanisidylporphinatoiron(II) complexes investigated in this study (Table I). The frequency depended upon the amine and increased in the order imidazole < pyridine ~ pyrrolidine, piperidine < morpholine. (One sample of the imidazole complex had two peaks, at 1966 and 1927 cm^{-1}, but had a Mössbauer spectrum identical with that of a sample which showed only one peak, at 1966 cm^{-1}.) Imidazole is the strongest σ donor of these amines, which leads

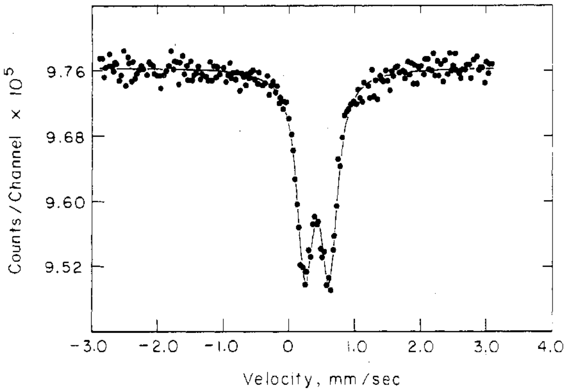

Figure 1. Mössbauer spectrum of PMXPPFe·Im·CO at 298 K.

to increased electron density on the iron. This strengthens the π bond between iron and carbon monoxide, and, as Alben and Caughey[3] pointed out, the stronger the Fe→CO π bond, the lower the CO stretching frequency. Morpholine appears to be the weakest σ donor. The weakness of both morpholine and piperidine as σ bases toward heme (despite their large pK_a's) is clearly due to steric effects as Hoard has definitely shown in his discussion of the crystal structure of bis(piperidine)-*meso*-tetraphenylporphinatoiron(II).[7] Steric effects may also play a role in heme binding to the sp^3 nitrogen of pyrrolidine. Thus, there is no need to invoke π donation by imidazole to low-spin iron(II)[8] (with its already filled π-bonding d orbitals) to explain the base strength of imidazole vs. piperidine.

The CO frequency of carbonylpyridinetetraphenylporphinatoiron(II) has been reported as 1975 cm^{-1}.[4]

All of the carbonyls gave sharp, well-resolved quadrupolar split doublets at room temperature (Table I). A representative spectrum is shown in Figure 1. The isomer shifts were equal, within experimental error, and averaged +0.46 mm/s. This value is about 0.2 mm/s smaller than the average of the bis(amine) hemochromes.[6] Both the bis(amine) and carbonylamine hemochromes contain low-spin iron(II); such a decrease in the isomer shift must be due to a decrease in d-electron density on the iron, arising from strong Fe→CO π bonding and the weaker Fe←CO σ bonding than Fe←amine σ bonding.

The quadrupole splittings, 0.4–0.6 mm/s, are quite small for hemochromes. Because of the strong electric field provided by the porphine dianion, very strong electric fields must be provided by the axial ligands in order for the iron to approach cubic symmetry. Carbon monoxide provides a much stronger electric field than do amines and significantly reduces the >1.0-mm/s splittings found for the bis(amine) hemochromes.[6] The splittings directly parallel the CO stretching frequencies.

For carbonyl-1-methylimidazole-*meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl)porphinatoiron(II) at 4.2 K, δ = 0.27 and Δ = 0.27 mm/s.[5]

Several carbonylamine complexes of iron(II), which are structurally somewhat related to the carbonyl hemochromes, have been investigated by Mössbauer spectroscopy. These have been mainly bis(dioximate) complexes. They show a similar decrease in both δ and Δ for the carbonylamine from the bis(amine) values: e.g., for *trans*-[Fe(niox)$_2$ImCO], δ = 0.34 and Δ = 0.77 mm/s at 77 K; for *trans*-[Fe(niox)$_2$Im$_2$], δ = 0.54 and Δ = 1.30 mm/s at 77 K[9] ("niox" indicates the 1,2-cyclohexanedione dioximate anion). Otherwise, they are not very comparable to the hemochromes as they have much smaller isomer shifts and much larger quadrupole splittings. Shifts of 0.17–0.28 mm/s and splittings of 1.77–2.16 mm/s, at 298 K, have been measured by Morpurgo and Mosini[10] for several *trans*-carbonyl(substituted pyridine)bis(dimethylglyoximato)iron(II) complexes.

Table II. Reported Mössbauer Data on Carbonyl Hemoproteins

Carbonyl compd	Temp, K	δ,[a] mm/s	Δ, mm/s	Ref
Hemoglobin	297	0.54	0.40	*b*
	195	0.44	0.36	*c*
	4	0.52	0.36	*c*
Myoglobin	77	0.46	0.28	*d*
RR cytochrome *cc*′	205	0.43	0.36	*e*
	4.6	0.47	0.36	*e*
C cytochrome *cc*′	205	0.42	0.28	*e*
	4.6	0.46	0.28	*e*
C cytochrome c_{552}	205	0.39	0.37	*e*
	77	0.43	0.38	*e*
Cytochrome P-450$_{\text{cam}}$	200	0.51	0.34	*f*
	4.2	0.52	0.36	*f*
JR peroxidase	195	0.43	0.21	*g*
	77	0.58	0.21	*g*
Chloroperoxidase	4.2	0.55	0.52	*f*

[a] Relative to sodium nitroprusside; all are positive. [b] J. E. Maling and M. Weissbluth, *Solid State Biophys.*, 327–368 (1969). [c] G. Lang and W. Marshall, *Proc. Phys. Soc., London*, 87, 3–34 (1966). [d] A. Trautwein, H. Eicher, A. Mayer, A. Alpen, M. Waks, J. Rosa, and Y. Beuzard, *J. Chem. Phys.*, **53**, 963–967 (1970). [e] T. Moss, A. J. Bearden, R. G. Bartsch, and M. A. Cusanovich, *Biochemistry*, 7, 1583–1590 (1968). [f] P. M. Champion, E. Munch, P. G. Debrunner, P. F. Hollenberg, and L. P. Hager, *ibid.*, **12**, 426–435 (1973). [g] Y. Maeda, *J. Phys. Soc. Jpn.*, **24**, 151–159 (1968).

Considerable Mössbauer data have been measured for carbonyl hemoproteins. Some of these data are shown in Table II. The average isomer shift at ~200 K is +0.44 mm/s, and the quadrupole splittings, which are temperature independent, average 0.33 mm/s. Japanese radish (JR) peroxidase carbonyl has an exceptionally small splitting, and chloroperoxidase carbonyl has an exceptionally large splitting; both of these however are unusual hemoproteins in other respects as well.

The cytochromes contain a methionine sulfur in an axial position along with a histidine imidazole. It is probably the iron–sulfur bond which breaks in forming the carbonyl, for those cytochromes which do react, since the splittings of the cytochrome carbonyls are very close to the 0.36 mm/s found for the simple carbonylimidazole hemochrome.

For carbonylhemoglobin and carbonylmyoglobin, V_{zz} is positive.[11,12] It is assumed that V_{zz} is positive for the simple carbonyl hemochromes listed in Table I, although the sign was not experimentally determined for any of these. Both the sign and magnitude of the quadrupole splittings of carbonyl hemoproteins have been treated theoretically by Trautwein et al.[12] and Halton.[13]

Acknowledgment. This research was supported in part by Grant No. 1 RO1 AM16995-01A1 BBCB, National Institutes of Health.

Registry No. PMXPPFe·morph·CO, 59711-65-8; PMXPPFe·pip·CO, 59711-66-9; PMXPPFe·py·CO, 59711-67-0; PMXPPFe·pyrr·CO, 59711-68-1; PMXPPFe·Im·CO, 59711-69-2; PMXPPFe·2morph, 59711-70-5; PMXPPFe·2pyrr, 59711-71-6; PMXPPFe·2pip, 59711-72-7; PMXPPFe·2py, 59711-73-8; PMXPPFe·2Im, 59711-74-9; PMXPPFeCl, 59711-75-0.

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Monothio-β-diketonates of Lanthanides. 2. 3-Mercapto-1,3-diphenylprop-2-en-1-one Chelates of Lanthanides

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Received August 29, 1975 AIC50646U

Lanthanide complexes derived from sulfur donors are expected to be weak because of the large ionic radii of the metal ions and the lower electronegativity of the donors. Dutt et al.[1] first indicated the formation of lanthanide chelates of monothiobenzoylacetone in solution. Subsequently, Brown et al.[2] and Siddall et al.[3] isolated both tris- and tetrakis(dialkyldithiocarbamates) of lanthanides through careful choice of the reaction conditions. Characterization of the tetrakis chelates of dialkyl dithiophosphinates has been made quite recently by Pinkerton.[4] We have investigated the solvent extraction behavior[5] of Nd(III) with monothiothenoyltrifluoroacetone (HSTTA) and the synergistic extraction[6] with some neutral donors. These studies have established that the species extracted in the organic phase have the composition $\mathrm{Nd(STTA)_3}$ and $\mathrm{Nd(STTA)_3A}_n$ (n = 1, dipyridyl; n = 2, tri-*n*-octylphosphine oxide, tri *n*-butyl phosphate). Also it has been shown that although $\mathrm{Nd(STTA)_3}$ is much less stable than $\mathrm{Nd(TTA)_3}$, the mixed formation constants ($\beta_{3,n}$) of $\mathrm{Nd(STTA)_3A}_n$ are greater than the corresponding TTA complexes (HTTA = thenoyltrifluoroacetone). Here we wish to report the facile preparation of a series of tetrakis, tris, and mixed tetrakis complexes of 3-mercapto-1,3-diphenylprop-2-en-1-one (monothiodibenzoylmethane, HSDBM) of lanthanides.

Experimental Section

Materials. Hydrated lanthanide perchlorate crystals were prepared from the lanthanide oxides (99.9% pure, supplied by Johnson Matthey). HSDBM was prepared by a modification[7] of the procedure adopted by Chaston et al.[8]

Preparation of Lanthanide Chelates. (i) $\mathrm{Ln(SDBM)_3{\cdot}H_2O}$. To a stirred ethanolic solution (30 ml) containing 1 mmol of the hydrated lanthanide perchlorate and 3 mmol of HSDBM, 3 ml of 1 M sodium hydroxide solution was added during a period of 30 min. The solution was filtered, and on removal of the solvent under reduced pressure a glassy mass was obtained. This was thoroughly stirred with petroleum ether (bp 40–60 °C), and the solvent was decanted off. On repetition of this operation for several times a solid mass free of HSDBM (since the ligand is highly soluble in petroleum ether) was obtained. The product was extracted with minimum volumes of chloroform (any unreacted lanthanide perchlorate and sodium perchlorate formed was thus removed) and filtered, and the filtrate was concentrated under reduced pressure. On cooling, a crystalline product in ~60% yield was obtained.

(ii) $\mathbf{Q[Ln(SDBM)_4]}$ (Q = Quaternary Ammonium Ions of Piperidine, Morpholine, and Pyrrolidine). To a stirred ethanolic solution containing 1 mmol of the hydrated lanthanide perchlorate and 4.2 mmol of HSDBM, an ethanolic solution of heterocyclic base (4.2 mmol) was added slowly. The mixture was stirred for 30 min, was cooled in an ice chest for 3 h, and was then filtered through a glass frit. The compound was washed successively with water, with a small volume of ethanol, and freely with petroleum ether. The product (0.5 g) was dissolved in 20 ml of a 1:1 acetone–methanol mixture, the mixture was filtered, and the filtrate was concentrated to ca. 8 ml. On cooling (below 0 °C), shining needle-shaped crystals deposited. Alternatively, 0.5 g of the compound was dissolved in benzene, the mixture was filtered and cooled to 10 °C, and the compound was precipitated by slow addition of petroleum ether (bp 40–60 °C); yield ~65%.

(iii) $\mathbf{Ln(SDBM)_3A}_n$ (A = 2,2′-Dipyridyl, *o*-Phenanthroline, n = 1; Pyridine *N*-Oxide, n = 2). An ethanolic solution of the hydrated lanthanide perchlorate (1 mmol) was slowly added into a stirred ethanolic solution containing 3 mmol of HSDBM, 1 mmol of dipyridyl (*o*-phenanthroline) or 2 mmol of pyridine *N*-oxide, and 3 ml of 1 M sodium hydroxide solution. The mixture was stirred additionally for 30 min, cooled, and then filtered. The product was washed with petroleum ether, water, and cold ethanol. The crude compound was recrystallized from a benzene–petroleum ether mixture; yield ~70%.

Analysis. C and H analyses were carried out in the Microanalytical Laboratory of this institute and CDRI, Lucknow, India. Sulfur was gravimetrically estimated as $\mathrm{BaSO_4}$. Lanthanides were volumetrically determined by EDTA titration using xylenol orange as the indicator.

Physical Measurements. Conductivity measurements of the compounds (ca. 1×10^{-3} M solutions in acetone) were carried out with a Philips PR 9500 conductivity bridge. Molecular weights of the compounds in chloroform and benzene were determined in a Mechrolab vapor-phase osmometer. Ir spectra (in Nujol mull) were recorded in the range 4000–250 cm^{-1} in a Perkin-Elmer 421 infrared spectrophotometer. Visible spectra of the Nd(III) compounds were recorded in a Spectro MOM 201 spectrophotometer in the concentration range 8×10^{-3}–1×10^{-2} M in acetone, chloroform, and benzene against the appropriate concentration of the ligand solution as blank. The oscillator strength (P) was determined using the relation

$$P = 4.31 \times 10^{-9} \left[\frac{9n}{(n+2)^2}\right] \epsilon_i(\nu)\, \mathrm{d}\nu$$

where n is the refractive index of the medium, ϵ is the molar extinction coefficient, and ν is the energy of transition in wavenumber. The area of a band was measured by a planimeter. X-ray powder patterns were obtained with a Philips PW 1008 x-ray diffraction unit, using a 114.6-mm Debye camera and Cu Kα radiation filtered through nickel.

Results and Discussion

Table I summarizes the analytical and characterization data of a few representative types of lanthanide chelates. Satisfactory analytical data were obtained for other lanthanide complexes. The compounds in general are fairly soluble in acetone, chloroform, and benzene and moderately soluble in methanol and ethanol. The pyrrolidinium compounds have appreciable solubility only in chloroform. The compounds are nonhygroscopic, are stable in air, and remain unchanged in composition for an indefinite period. Molecular weight determinations carried out in chloroform and benzene indicate that $\mathrm{Q[Ln(SDBM)_4]}$ type compounds remain undissociated in these solvents (Table I), whereas their molar conductances in acetone are consistent with 1:1 electrolytes. Similar observations have been reported[9] for a large number of lanthanide tetrakis(pivaloyltrifluoroacetonates) having different counterions. Powder diffraction data of $\mathrm{(pipH)[Nd(SDBM)_4]}$ and $\mathrm{(pipH)[Nd(DBM)_4]}$ reveal they are not isomorphous. The tetrakis chelates of Eu(III) in chloroform fluoresce on exposure to a mercury lamp.

Infrared spectra of SDBM chelates have the overall features expected from the work of Livingstone and co-workers[10] and Uhlemann et al.[11] However, some of their band assignments appear doubtful in the light of normal-coordinate analysis