

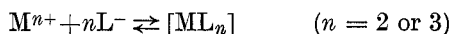
ON THE FORMULATION OF BIGUANIDE COMPLEXES

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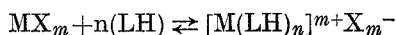
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It is accepted that biguanide $\text{H}_2\text{NC}(=\text{NH})\text{NHC}(=\text{NH})\text{NH}_2$ yields two series of complexes with metal ions,¹ formally:

(a) with the deprotonated ligand (L^-), to give an uncharged complex,



(b) with the parent ligand (LH), to give a charged complex,



Where the anion (X^-) is Cl , $\frac{1}{2}\text{SO}_4$, etc., no confusion as to the nature of the complex arises. However, where $\text{X}^- = \text{OH}$, a choice between the alternative formulations $[\text{ML}_n]_n \cdot n\text{H}_2\text{O}$ (I), and $[\text{M}(\text{LH})_n](\text{OH})_n$ (II), for the "complex base" is required and there is conflict in the literature on this point.¹⁻³ In drawing a distinction between (I) and (II), conductance methods cannot in general be employed as many biguanide complexes are either insoluble or, if soluble, hydrolyse in solution. Some indication of the correct formula for the complex bases can be obtained from the fact that they can be dehydrated easily to the anhydrous forms, i.e. to $[\text{ML}_n]$.

We have investigated the possibility of characterization and identification of the two series from electronic and vibrational spectra.

Comparisons of the electronic spectra of related tris-biguanide complexes of cobalt(III) and chromium(III) (Table 1) reveal small but definite band shifts to lower wave numbers for the spin-allowed transitions in passing from the charged to uncharged complexes. The position in the spectrochemical series occupied by deprotonated nitrogen chelates does not appear to have been studied. However, it is of interest to note that the shift can be rationalized in terms of the relationship between charge on the central ion and Δ values. Recently Watt *et al.*⁴ have reported marked changes in colour between the protonated and deprotonated forms of triethylenediamine osmium(III) complexes. We have not observed significant shifts on dehydrating the tris-chelated complex bases of chromium(III) and cobalt(III) (see Table 1). Hence formulation as (I) rather than (II) is supported.

We have also examined the infrared spectra of the above compounds and of the bis-chelated complexes of cobalt(II) and copper (II). The band positions observed in the region $1700\text{--}1400\text{ cm}^{-1}$ and assignments are listed in Table 2. Partial assignments

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¹ Ray, P., *Chem. Rev.*, 1961, **61**, 313.

² Ray, P., and Saha, H., *J. Indian chem. Soc.*, 1937, **14**, 670.

³ Ray, P., and Ghosh, S. P., *J. Indian chem. Soc.*, 1943, **20**, 295.

⁴ Watt, G. W., Summers, J. T., Potrafke, E. M., and Birnbaum, E. R., *Inorg. Chem.*, 1966, **5**, 857.

for biguanide sulphate have been reported previously⁵ but the complexes have not been examined. Our data show that the NH deformation frequencies are higher and the N-C-N stretching frequencies are lower for the complex salts than for the complex bases in each series. Further, on dehydration of the bases no spectral changes are observed, with the exception of a reduction in intensity for bands near 1630 cm^{-1} as would be expected on loss of water. We conclude that the complex bases should be formulated as hydrated uncharged complexes (I).

TABLE 1
REFLECTANCE SPECTRA OF BIGUANIDE COMPLEXES
LH = biguanide, $\text{C}_2\text{H}_7\text{N}_5$; L = $\text{C}_2\text{H}_6\text{N}_5^-$

Complex	Band Positions (cm^{-1}) and Assignments	
[CrL ₃] (anhydrous)	20000 ($^4A_{2g} \rightarrow ^4T_{2g}$)	26000 ($^4A_{2g} \rightarrow ^4T_{1g}$)
[CrL ₃] (hydrated)	19700	26000
[Cr(LH) ₃]Cl ₃	20700	27100
cf. [Cren ₃]Cl ₃ ^a	21850	28500
[CoL ₃] (anhydrous)	19600 ($^1A_{1g} \rightarrow ^1T_{1g}$)	26800 ^b ($^1A_{1g} \rightarrow ^1T_{2g}$)
[CoL ₃] (hydrated)	19700	27000 ^b
[Co(LH) ₃]Cl ₃	20200	27800 ^b
cf. [Coen ₃]Cl ₃ ^a	21400	29500

^a From Jorgensen, C. K., "Absorption Spectra and Chemical Bonding in Complexes." (Pergamon: London 1962.)

^b Band exhibited as shoulder.

TABLE 2
INFRARED SPECTRA OF BIGUANIDE COMPLEXES
LH = biguanide, $\text{C}_2\text{H}_7\text{N}_5$; L = $\text{C}_2\text{H}_6\text{N}_5^-$

Complex	NH def	OH + NH def	N-C-N str
[CrL ₃],hydrated		1630vs, 1624vs	1580vs, 1560vs, 1458vs
[Cr(LH) ₃]Cl ₃	1673vs(br), 1624m(sh)		1509s(br), 1406w
[CoL ₃],hydrated		1630vs, 1610vs	1590vs(sh), 1575vs, 1450vs(br)
[Co(LH) ₃]Cl ₃	1690vs(br), 1665vs(br), 1600(sh)		1450s(br), 1395s
[CoL ₃],hydrated		1608vs	1567vs, 1498vs, 1462w
[Co(LH) ₃]SO ₄	1661vs, 1631(sh)		1577sh, 1513, 1391w
[CuL ₂],hydrated		1625vs, 1605vs	1566vs, 1490sh, 1460vs, 1449vs
[Cu(LH) ₂]Cl ₂ ,hydrated	1686vs	1630w, 1610m	1545s, 1515sh, 1435w

Experimental

Complexes were prepared by published methods for the cobalt(II),³ copper(II),¹ chromium(III),⁶ and cobalt(III)⁷ biguanides.

Diffuse reflectance spectra were measured using a modified⁸ Unicam SP500 spectrophotometer. Infrared spectra were recorded on either a Perkin-Elmer 221 spectrophotometer with

⁵ Colthup, N. B., Daly, L. H., and Wiberly, S. C., "Introduction to Infrared Spectroscopy." (Academic Press: New York 1964.)

⁶ Ray, P., *Inorg. Synth.*, 1960, **6**, 68.

⁷ Ray, P., and Dutt, M. K., *J. Indian chem. Soc.*, 1939, **16**, 621.

⁸ Smith, P. W., and Wedd, A. G., *J. chem. Soc. (A)*, 1968, 1377.

prism grating interchange or a Grubb-Parsons Spectromaster, using Nujol or hexachlorobutadiene mulls. Vibrational assignments were made on the basis of published data for ethylenediamine,⁹ urea,¹⁰ and the guanidinium¹¹ ion, and confirmed by comparison of spectra before and after deuteration.

Acknowledgment

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⁹ Powell, D. B., and Sheppard, M., *Spectrochim. Acta*, 1961, **17**, 68.

¹⁰ Penland, R. B., Mizushima, S., Curran, C., and Quagliano, J., *J. Am. chem. Soc.*, 1957, **79**, 1575.

¹¹ Angell, C. L., Sheppard, N., Yamaguchi, A., Shimanouchi, T., Miyazawa, T., and Mizushima, S., *Trans. Faraday Soc.*, 1957, **53**, 589.