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Preliminary communication

Cis and *trans* effects and NMR correlations in organometallic cobaloximes

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Abstract

A study has been made of electronic *cis* and *trans* influences in cobaloximes of the type $[Co(dmgH)_2X(L)]$, where dmgH is dimethylglyoximato, L is 2,6-dimethylpyrazine or 3,5-lutidine, and X is an alkyl or inorganic anionic ligand. The downfield shifts of the methylic protons of the equatorial (dmgH) ligands in the ^1H NMR spectra are linearly related to the upfield shifts of the α-protons of L, and the shifts are correlated with the wavelength of the Co → dmgH charge transfer band in the ultraviolet. Such correlations have been previously observed only for non-organometallic cobaloximes, and explained in terms of the ring current produced by the delocalized π electrons of the metallacycles. The alkyl groups have the smallest effects on the chemical shifts of both the *cis* and *trans* ligand.

We recently reported some regularities in the NMR spectra of cobaloximes of the types $[Co(DH)_2XB]$ and $[Co(DH)_2LB]^+$, where DH = dimethylglyoximato (dmgH) or diphenylglyoximato (dpgH); X = Cl, Br, or CN; L = H_2O or PPh_3, and B = pyridine (py), 4-cyanopyridine, 2,6-dimethylpyrazine (dmp), pyridazine, or 3,5-dimethylpyrazole. The reported trends [1,2] are related to the mutual *cis* and *trans* influences of the ligands, as reflected in their NMR chemical shifts, and include (a) correlation of the ^1H NMR chemical shifts of the protons of the axial ligands B with those of the equatorial ligand DH, and (b) a multilinear correlation of the chemical shift of the protons in B with their position in the molecule and with the wavelength of the Co → DH charge transfer band.

The above spectral correlations have been rationalized in terms of ring-current effects by considering the isolobal relationship between a cobaloxime and an aromatic organic molecule such as the biimidazolato dianion [1]. Furthermore, the extent of the downfield shift of the cobaloxime methylic protons, has been suggested to be a measure of the π-acceptor/π-donor ability of the axial ligands B or X [2].

The purpose of the present work was to find out whether the previously reported trends also apply to organometallic cobaloximes. Thus, new members of the family

$[Co(dmgH)_2XB]$ have been obtained and studied, namely those with B = 2,6-dimethylpyrazine (dmp) or 3,5-lutidine (lut), and X = Cl, Br, CN, NO_2, N_3, CH_3, CH_2I, CH_2Br, C_2H_5, ^{i}Pr and ^{i}Bu.

The coordination shift $\Delta\delta = \delta(\text{complex}) - \delta(\text{free ligand})$ of the a protons of both dmp and lut, can be used as a measure of the *trans* influence of the axial X group, allowing us to extend the previously established series with the inclusion of alkyl groups. The decreasing order of upfield shifts induced for H_α of the *trans* ligand is as follows: $Cl \approx Br > NO_2 \approx N_3 > CN > CH_2I \geq CH_2Br > {}^{i}Bu \approx {}^{i}Pr \approx C_2H_5 \approx CH_3$. This *trans* influence is correlated with the *cis* one experienced by the methyl groups of the equatorial dmgH ligands: the downfield shifts of the corresponding signals follow the same order. The β-methyl groups of lut and dmp, as well as the γ proton of lut, are much less affected by changes in the *trans* ligand, in agreement with their greater distances from the metallabicycle.

The influence of the X ligand on the chemical shifts of the *cis* (Me of dmgH) and *trans* (H_α of lut or dmp) ligands are opposite in sign but of the same magnitude. This contrasts with the usual trends in the NMR spectra of transition metal complexes or organometallic compounds, for which *trans* influences are much more important than the *cis* ones. This difference can be attributed to the fact that in most complexes the *cis* and *trans* influences on the chemical shifts arise from an inductive effect, whereas in the present case the main factor seems to be the ring-current associated with an aromatic-like metallabicyclic system [1,2].

The behaviour of the organometallic cobaloximes represents a simple extension of that previously reported for non-organometallic cobaloximes [1,2]. The coordination shifts corresponding to the H_α resonances are apparently related to the covalence of the metal–*trans* ligand bond, and so the halomethyl complexes give rise to more negative coordination shifts than the methyl ones, and the cyano ligand appears in a region intermediate between those of the organometallic and the inorganic ligands.

A further interesting correlation is that relating the ^{1}H NMR chemical shifts to the wavelength of the Co → dmgH charge transfer band. When only values of λ for which the assignment is clear are used, along with the corresponding coordination shifts for the α proton of dmp or lut, a fair linear correlation is found, $\Delta\delta(H_\alpha) = 3.51 - 0.0150\lambda$ (for 12 experimental points; regression coefficient 0.95; standard error of estimate = 0.035 ppm). This equation is similar to that previously reported [2] except for the absence of the positional coordinates of the α proton in eq. 2. X-ray structural studies of these compounds are being carried out in order to check whether the structure-NMR spectra correlation previously found for inorganic cobaloximes holds for the organometallic species.

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References

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