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Effect of Oxygen-by-sulfur and Sulfur-by-selenium Donor Atom Replacement on ^{59}Co NMR Chemical Shifts in Cobalt(III) Tris-chelates of Acylchalcogenoureates

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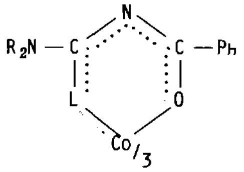
For an exact comparison of the influence of donor atoms on ^{59}Co NMR chemical shifts, one has to study isostructural complexes. This requirement is not easily fulfilled because of difficulties in the preparation of such complexes. Only in a few cases has corresponding study been made. Thus, oxygen-by-sulfur donor atom replacement was investigated in tris(β-diketonato)cobalt(III) complexes [1], while sulfur-by-selenium replacement was investigated in tris(dithiocarbamato)cobalt(III) complexes [2] and in dihalogenobis[(*o*-(methylthio)phenyl)diphenylphosphine]cobalt(III) halogenide complexes [3]. Phosphorus-by-arsenic and arsenic-by-antimony donor atom replacement was investigated in *o*-phenylenebis(dimethylphosphine) complexes of cobalt(III) [3, 4].

We report here the first example of the effect of oxygen-by-sulfur and sulfur-by-selenium donor atom replacement on the ^{59}Co NMR chemical shifts in the isostructural cobalt(III) complexes. The effect was investigated in tris(*N*,*N*-dialkyl-*N*′-benzoyl-(oxo/thio/selenoureato)cobalt(III) complexes (Scheme 1).



R = Et, n-Pr
L = O, S, Se

Scheme 1.

TABLE 1. ^{59}Co NMR chemical shifts (δ, ppm) and line-width ($\Delta\nu_{1/2}$, kHz) of *fac*-[Co(OC(Ph)NC(NR$_2$)L)$_3$] complexes (R = Et, n-Pr; L = O, S, Se)

L	R	$\delta(^{59}\text{Co})^{a}$	$\Delta\nu_{1/2}$
O	ethyl	13380	0.3
S	ethyl	8538	0.3
S	n-propyl	8543	0.3
Se	n-propyl	9005	0.4

^{a}±50 ppm; relative chemical shifts within the series are accurate to ±2 ppm.

As is seen from the results given in Table 1, the oxygen-by-sulfur donor atom replacement results in a −1650 ppm chemical shift per donor atom, while the sulfur-by-selenium replacement causes a +155 ppm chemical shift per donor. The trend in the chemical shift changes upon the donor atom replacement agrees with that previously observed for the oxygen-by-sulfur [1] and the sulfur-by-selenium [2–4] replacement. What is perhaps unexpected is that the chemical shift of the sulfur-by-selenium replacement depends very much on the kind of isostructural complexes investigated. Thus, a replacement chemical shift of +480 ppm per donor is observed for dihalogenobis[(*o*-(methylthio)phenyl)-diphenylphosphine]cobalt(III) ion [3], but a shift of only +10 ppm is found for the tris(dithiocarbamato)-cobalt(III) complex [2].

The observed trend in donor atom influence on ^{59}Co NMR chemical shifts (O > Se > S) could be rationalized by noting that the shifts are influenced both through metal–ligand bond covalency and d-electron excitation energy, as they are proportional to $\beta_{35}/\Delta E$ [5]. The nephelauxetic ratio (β_{35}) generally diminishes in the order O ≫ S > Se [6], while for the excitation energy (ΔE) the ordering is O ~ S > Se [7]. Therefore, the nephelauxetic and spectrochemical influences on the chemical shift run in the opposite directions when going from sulfur to selenium. Obviously, the spectrochemical influence predominates since the higher chemical shifts are observed for the selenium donor complexes. However, the balance of the two opposite influences is rather sensitive to the structure of the complex.

Experimental

For syntheses of the complexes see ref. 7. For NMR measurements, chloroform solutions (1×10^{-2} mol/dm^3) of the complexes were used. The ^{59}Co NMR spectra were recorded on a Brücker SXP-100 spectrometer operating on 21.5 MHz at room temperature. Chemical shifts were determined using aqueous K$_3$[Co(CN)$_6$] solution as an external standard.

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