Inorganica Chimica Acta, *87* (1984) L37–L39

Synthesis and ^{59}Co NMR Study of the Mixed Oxo/Thiotris(β-diketonato)cobalt(III) Complexes

N. JURANIĆ

Department of Chemistry and Physical Chemistry, University of Belgrade, P.O. Box 550, 11001 Belgrade, Yugoslavia

Received March 15, 1984

Introduction

NMR chemical shifts of the transition metal ions in octahedral spin-paired d^6 complexes are influenced by both spectrochemical and nephelauxetic properties of ligands [1]. The combined effect of these properties makes difficult the interpretation of metal chemical shifts in mixed ligand complexes. Therefore, one may look for the series of mixed ligand complexes having small variation in spectrochemical properties, but large variations in nephelauxetic properties of ligands (or *vice versa*), which would enable separate studies of the above effects. In fact the corresponding study of the effect of ligand spectrochemical properties on metal chemical shift has been successfully accomplished in mixed ligand complexes of the type $CoN_{6-x}O_x$ [2]. Contrary to this, a corresponding study of the effect of ligand nephelauxetic properties is still to be done. For this purpose we find a $CoO_{6-x}S_x$ series of mixed ligand complexes very promising. Namely, oxygen coordinated ligands and sulphur coordinated ligands occupy practically the same position in the spectrochemical series of ligands, while covalency of the metal–ligand bond is much higher for sulphur coordinated ligands [3].

Cobalt(III) complexes of the CoO_6 and CoS_6 types are quite numerous, yet mixed ligand, $CoO_{6-x}S_x$ type complexes, are difficult to prepare. The only known complexes are those belonging to the CoO_3S_3 chromophore, and they have been obtained using bidentate ligands chelated through oxygen and sulphur [4–7]. Complex of the CoO_5S chromophore is reportedly formed in the course of the tris(dithioacetylacetonato)cobalt(III) complex synthesis [8]. The difficulty of preparing mixed ligand complexes is probably due to the lability of the cobalt–oxygen bond in comparison with cobalt–sulphur bond, which causes disproportionation of such complexes. Since tris(β-diketonato)cobalt(III) complexes seems to form the most stable CoO_6 chromophore we undertook preparation of mixed oxo/thio-tris(β-diketonato)cobalt(III) complexes. As a result we report here the first successful synthesis of $Co(III)O_5S$ and $Co(III)O_4S_2$ type complexes. We also made a ^{59}Co NMR study of the $CoO_{6-x}S_x$ (x = 0–3) chromophores.

Results and Discussion

Our initial attempts to prepare mixed oxo/thio-tris(β-diketonato)cobalt(III) complexes, using various mixtures of acetylacetone (acacH) and monothiodibenzylmethane (PhacPhSacH) in reaction with potassium tricarbonatocobalt(III) complex, all failed. In all cases a complete amount of PhacPhSac ligand produced only the [Co(PhacPhSac)$_3$] complex. However, we accomplished the synthesis of the CoO_5S and CoO_4S_2 type complexes by initiating, at elevated temperature, ligand exchange between [Co(acac)$_3$] and [Co(PhacPhSac)$_3$] complexes in acetylacetone. In this reaction mixed ligand com-

TABLE I. Proton Chemical Shifts of the Acetylacetonato Ligand and ^{59}Co Chemical Shifts in the studied Complexes.

Type	Complex	$\delta(^1H)$/ppm		$\delta(^{59}Co)$ ppm
		–CH–	–CH_3	
CoO_6	[Co(PhacPhac)$_3$]			12530
	[Co(acac)$_3$]	5.46	2.15	12630
CoO_5S	[Co(acac)$_2$(PhacPhSac)]	5.45	2.00	11350
		5.58	2.04	
			2.08	
			2.44	
CoO_4S_2	*cis*(S)-C_1-[Co(acac)(PhacPhSac)$_2$]	5.53	1.91	9450
			2.33	
CoO_3S_3	*facial*(S)-[Co(PhacPhSac)$_3$]			7580

0020-1693/84/$3.00

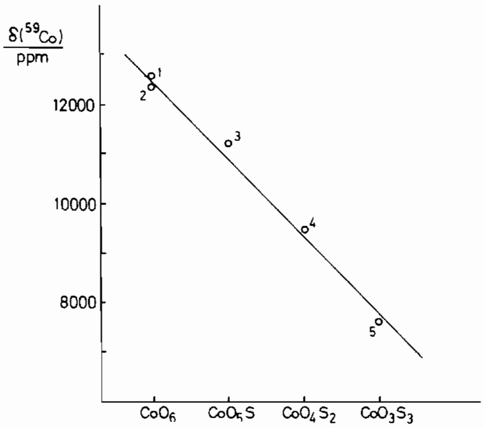

Fig. 1. Additivity of the effect of the gradual oxygen by sulphur replacement on the ^{59}Co chemical shifts in the studied complexes; 1: [Co(acac)$_3$], 2: [Co(PhacPhac)$_3$], 3: [Co(acac)$_2$(PhacPhSac)], 4: *cis*(S)-C$_1$-[Co(acac)(PhacPhSac)$_2$], 5: *fac*(S)-[Co(PhacPhSac)$_3$].

plexes [Co(acac)$_2$(PhacPhSac)] and *cis*(S)-C$_1$-[Co(acac)(PhacPhSac)$_2$] were both obtained at a yield of 10%. It was noted that on prolonged standing in solution at room temperature they undergo disproportionation to the starting complexes.

Obtained complexes have been identified by elementary analysis and PMR spectra. Especially instructive were the resonances of the acetylacetonato ligand (Table I). In the [Co(acac)(PhacPhSac)$_2$] complex methyl groups of the acetylacetonato ligand are non-equivalent. Therefore, this complex has C$_1$-symmetry, which shows that this has to be *cis*-(S)-C$_1$ isomer. Two other isomers, *cis*(S)-C$_2$ and *trans*(S), obviously are not formed in the reaction in a significant yield. It seems, therefore, that the *trans*(S) configuration is highly unfavorable, since [Co(PhacPhSac)$_3$] complex is also obtained only as *facial* (S) isomer.

The newly synthesized complexes, together with the already known complexes [Co(acac)$_3$], [Co(PhacPhac)$_3$] and *facial*(S)-[Co(PhacPhSac)$_3$], form the series $CoO_{6-x}S_x$ ($x = 0$–3) which has been studied by ^{59}Co NMR. As is seen in Table I, ^{59}Co chemical shifts are very sensitive on the replacement of oxygen by sulphur ligator. Effect of the gradual oxygen by sulphur replacement is almost additive (Fig. 1) and causes, on average, an upfield shift of 1700 ppm. This feature of ^{59}Co NMR spectroscopy is likely to be used for monitoring of oxygen by sulphur replacement in $CoO_{6-x}S_x$ type complexes.

Observed ^{59}Co chemical shift variations are properly ascribed to the changes of cobalt nucleus paramagnetic shielding term. This term may be put into the form [1]: $\sigma^p = -32\mu_B^2 < r^{-3} >_{d_F} \eta/\Delta E$. The form in which all specific influences of metal–ligand bond on the paramagnetic shielding are contained in two (mutually independent) quantities: the circulation-removing ratio η (which is mainly proportional to the nephelauxetic ratio [1]), and d–d electronic transition energy. Therefore, changes in the circulation-removing ratio (which is sensitive on metal–ligand covalency) have to account for the observed ^{59}Co chemical shift variations. Observed additivity of the effect of the gradual oxygen by sulphur replacements shows that the circulation-removing ratio in the studied complexes obeys the Rule of Average Environment. Further investigations are necessary to prove whether so simple a rule is generally applicable to the effect of metal–ligand bond covalency on metal ion chemical shifts in mixed ligand complexes. If it does, it allows relatively precise prediction of these shifts and hence their use for the identification of mixed ligand complexes.

Experimental

For the ligand exchange reaction 2 g of [Co(acac)$_3$] and 1 g of [Co(PhacPhSac)$_3$] were dissolved in acetylacetone (20 cm^3) and heated to boiling. After two minutes of boiling the mixture was left to cool to the room temperature and then acetylacetone was evaporated by the stream of hot air. Dry residue was dissolved in benzene and transferred to a silicagel (Merck 20–230 mesh) column (2 X 50 cm) and eluated with benzene. The first eluated fraction was the unreacted [Co(PhacPhSac)$_3$] complex. The second (brown-black) and third (darkly brown-green) eluated fractions were shown to contain *cis*(S)-C$_1$-[Co(acac)(PhacPhSac)$_2$] and [Co(acac)$_2$(PhacPhSac)] complexes, respectively. The mixed ligand complexes were recovered by evaporating corresponding fractions to dryness. Yield about 0.1 g of each complex.

Anal. Calcd. for $C_{35}H_{29}S_2O_4Co$: C, 66.04; H, 4.56; S, 10.00. Found: C, 65.84; H, 4.89; S, 10.01.

Calcd. for $C_{25}H_{25}SO_5Co$: C, 60.48; H, 5.04; S, 6.45. Found: C, 60.06; H, 5.17; S, 5.94.

^{59}Co chemical shifts were determined at room temperature on a Bruker NMR spectrometer operating at 21.5 MHz using 0.5 molar solutions of complexes in benzene. Shifts are reported relative to the external standard of aqueous Na$_3$[Co(CN)$_6$].

Acknowledgements

This work was supported by the Serbian Republic Research Fund. The author is grateful to Professor M. B. Ćelap for helpful discussions in the course of preparation of the manuscript.

References

1 N. Juranić, *Inorg. Chem., 22,* 521 (1983).
2 N. Juranić, M. B. Ćelap, D. Vučelić, M. J. Malinar and P. N. Radivojša, *J. Magn. Reson., 35,* 319 (1979).
3 C. K. Jørgensen, *Inorg. Chim. Acta Rev., 2,* 65 (1968).
4 M. P. Schubert, *J. Chem. Soc. Ser. A, 55,* 3336 (1933).
5 E. Uhlemann, G. Klase and H. Müller, *Z. Naturforschung, 19b,* 962 (1964).
6 L. Beyer, E. Hoyer, H. Hennig, R. Kirmse, H. Hartmann and J. Liebscher, *J. Prakt. Chem., 317,* 829 (1975).
7 M. Leitheisar and D. Coucouvanis, *J. Inorg. Nucl. Chem., 39,* 811 (1977).
8 G. A. Meath and R. L. Martin, *J. Chem. Soc., Chem. Commun.,* 951 (1969).