CHEMISTRY LETTERS, pp. 117-118, 1978. Published by the Chemical Society of Japan

TRANSITION METAL COMPLEXES WITH A NEW SEXADENTATE β-KETOAMINATO SCHIFF BASE LIGAND

Katsuma HIRAKI, Masayoshi ONISHI, Kazutoshi HAMADA,
and Hitoshi OGATA
Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Bunkyo-cho, Nagasaki 852

A new Schiff base, N,N',N''-1,3,4-neopentanetriyltris(4-imino-2-pentanone) was prepared from acetylacetone and 1,1,1-tris(aminomethyl)ethane. This Schiff base served as a trivalent sexadentate N_3O_3 ligand, which formed mononuclear six-coordinated neutral complexes with Co(III) and Fe(III) ions.

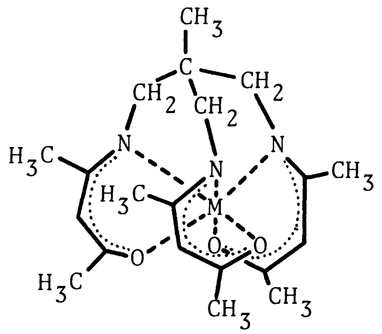
It has been reported that 1,1,1-tris(aminomethyl)alkane yielded Schiff bases, *e.g.*, 1,1,1-tris(pyridine-2-carboxaldiminomethyl)ethane$^{1)}$ and N,N',N''-tris(salicylidene)-2-aminomethyl-1,3-diaminopropane,$^{2)}$ which served as sexadentate ligands with C_3 symmetry. These ligands were coordinated to transition metal ions to form pseudooctahedral complexes.$^{1,2)}$

We now wish to report the synthesis and characterization of N,N',N''-1,3,4-neopentanetriyltris(4-imino-2-pentanone) (H_3nptp) derived from 1,1,1-tris(aminomethyl)ethane (tame)$^{3)}$ and acetylacetone, and of transition metal complexes with this Schiff base.

A benzene solution of tame was prepared from tame·3HCl$^{3,4,5)}$ (0.72g) and powdered KOH. The solution was slowly added to acetylacetone (13ml) with stirring, and the mixture was heated under reflux for 1/2 hr. The solvent was removed *in vacuo*, and the residue was recrystallized from benzene – hexane (1:10) mixture to give pale yellow needles of H_3nptp, 0.85g (74%), mp 89.5 – 90.5°C. Found : C, 65.82; H, 9.35; N, 11.53%. Calcd for $C_{20}H_{33}N_3O_3$: C, 66.09; H, 9.15; N, 11.56%.

The IR spectrum of H_3nptp showed three strong bands at 1610, 1580, and 1520cm^{-1}, which were characteristic of a tautomeric β-ketoamine Schiff base. The NMR spectrum in $CDCl_3$ showed a doublet at δ 3.27ppm with J=6Hz, which was ascribed to methylene protons in the tame moiety coupled with a proton attached to nitrogen.

An ethanol solution of H_3nptp (0.59g) was added dropwise to an ethanol solution of anhydrous cobalt(II) chloride (0.21g). Sodium ethoxide (0.71g) was added, and oxygen gas was bubbled into the solution for 1 hr. After the solvent was evaporated *in vacuo*, the residue was extracted with dichloromethane. The extract was concentrated to *ca*. 5ml and mixed with hexane (15ml). Upon cooling at −20°C, brown-black plates precipitated. The resulting crystals were collected, washed with hexane and dried *in vacuo* to give N,N',N''-1,3,4-neopentanetriyltris(4-imino-2-pentanonato)cobalt(III) [Co(nptp)], 0.31g (46%), mp 232 − 234°C (dec). Found : C, 56.96; H, 7.30; N, 9.92%; MS *m/e*, 419 (M^+). Calcd for $C_{20}H_{30}N_3O_3Co$: C, 57.28; H, 7.21; N, 10.02%; mol wt, 419.42.



The IR spectrum of [Co(nptp)] showed two strong bands at 1580 and 1500cm^{-1}, which were attributed to a β-ketoaminato ring of the complex. The NMR spectrum in DMSO-d_6 showed an AB pattern with δ_a 2.78, δ_b 2.93ppm, and J_{ab}=13Hz. This pattern was assigned to non-equivalent methylene protons in the tame moiety, indicating that [Co(nptp)] had a pseudooctahedral structure with C_3 symmetry. At temperatures above 130°C, these signals began to broaden gradually. However, coalescence of the AB pattern owing to trigonal twisting was not observed even at 176°C.

N,N',N''-1,3,4-Neopentanetriyltris(4-imino-2-pentanonato)iron(III) [Fe(nptp)] was prepared from anhydrous iron(III) chloride with a method similar to that stated above and purified with crystallization from hexane to afford deep purple needles in 22% yield, mp 210 − 211°C (dec). Found : C, 57.59; H, 7.45; N, 9.93%; MS *m/e*, 416 (M^+). Calcd for $C_{20}H_{30}N_3O_3Fe$: C, 57.70; H, 7.26; N, 10.09%; mol wt, 416.33.

[Fe(nptp)] sublimed at 130°C (10^{-3}mmHg) accompanying partial decomposition. The IR spectrum was similar to that of [Co(nptp)].

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(Received November 21, 1977)