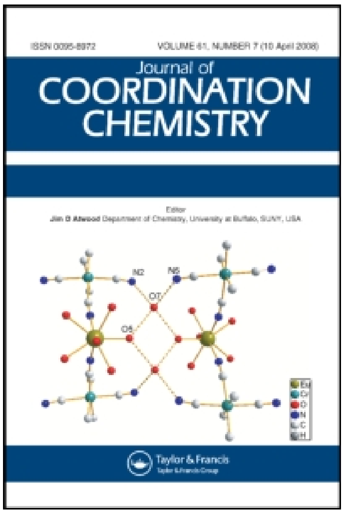

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THE MOLECULAR AGGREGATION OF ANHYDROUS *bis*-(2,4-PENTANEDIONO)-NICKEL(II) IN CCl_4 SOLUTION

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Although the trimeric nature of *bis*-(2, 4-pentanediono)-nickel(II), $Ni(AA)_2$, in the solid state has been conclusively established by X-ray crystallography[1] the molecular aggregation of $Ni(AA)_2$ in solution is less certain. It had been concluded from earlier ebullioscopic measurements[2] on benzene and CCl_4 solutions of anhydrous $Ni(AA)_2$ and cryoscopic measurements[3] performed on benzene solutions that the trimeric aggregation was maintained in solution. These techniques give the number-average molecular weight, M_n. However, a recent determination of the weight-average molecular weight, M_w, of $Ni(AA)_2$ in CCl_4 solution, employing the Brillouin light-scattering technique, gave a value for M_w of 2220, whereas the molecular weight of the trimer is only 771.[4] From these data $Ni(AA)_2$ was presumed to exist in CCl_4 solution as a broad distribution of oligomers such that the value of the number-average molecular weight, M_n, would be near the value for the trimer but population of higher molecular weight species would be such as to raise the value of M_w to such a large value. Mathematically, such an argument is tenable since the value of M_n is most sensitive to the lower molecular weight species present while the value of M_w is sensitive to the presence of species of higher molecular weight.

However, from a structural point of view, this result did not seem entirely plausible. The trimer structure is unique (as pointed out long ago[5]) in providing exact utilization of the available number of oxygen atoms per $Ni(AA)_2$ unit in a chain of face-sharing octahedra. It is, of course, possible that in solution the $Ni(AA)_2$ units might redistribute themselves into chains in which only some octahedra share faces and other share edges, as in the $[Co(AA)_2]_4$ molecule. However, there is the additional problem that the M_n and M_w values can be reconciled only by assuming that there are some very large oligomers present together with small ones, but very few oligomers of intermediate size. It would seem more reasonable to suppose that if the system really is polydisperse, with trimers predominating, there would be a steadily decreasing population of the increasingly large oligomers.

We felt that this problem merited further investigation, and therefore undertook to redetermine the value of M_n as accurately as possible by vapor osmometry, using the same solvent, CCl_4, as had been used for the M_w measurements.

Anhydrous $Ni(AA)_2$ was prepared[5] from $Ni(AA)_2 \cdot 2H_2O$ (Alfa Inorganics). A Hewlett-Packard Vapor Pressure Osmometer, Model 302, was calibrated with CCl_4 solutions of benzil. The solutions of $Ni(AA)_2$ were prepared and handled in an atmosphere of prepurified nitrogen. A similar set of solutions of the monomeric complex, $Cr(AA)_3$ (J. T. Baker Chemical Company), was prepared as a "blank" run.

For each compound the difference in resistance, ΔR (ohms), between two thermistors was measured in triplicate at five concentrations (C,$g/1$). The data for $Ni(AA)_2$ are as follows, $\Delta R(C)$: 20.3 ± 1.6 (51.1), 14.56 ± 0.16 (33.7), 10.13 ± 0.07 (22.3), 6.23 ± 0.10 (14.7), 4.52 ± 0.02 (9.7). A plot of ΔR vs. C for each compound demonstrated that ΔR was a linear function of C for *each* compound over the concentration range examined. If the $Ni(AA)_2$ system were polydisperse such a linear relationship would be surprising since the value of M_n should change upon varying the solute concentration. A linear least-squares fit to these data gave the following expressions:

$$\Delta R\text{benzil} = (1.492 \pm 0.053)\,C + 1.992 \pm 0.471$$
$$\Delta R\text{Cr(AA)}_3 = (1.009 \pm 0.010)\,C + 1.280 \pm 0.093$$
$$\Delta R\text{Ni(AA)}_2 = (0.427 \pm 0.016)\,C + 0.290 \pm 0.348$$

Using the graphical-gradient procedure,[6] the values for M_n were calculated readily from the slopes of the above curves, with the following results:

$Cr(AA)_3$, 311 ± 11 (349 theory); $Ni(AA)_2$, 735 ± 38. The value of M_n for $Ni(AA)_2$ is within one standard deviation (σ) of the calculated value for $[Ni(AA)_2]_3$.

This result for M_n is very difficult to reconcile with the reported value of M_w. Even if we assume that the experimental value of M_n might be low by 3σ, i.e., if we allow that M_n might be 850, and assume further that as much as 5% of the solute could be present as species of high molecular weight, it is necessary to assign these species a mean weight of 5143 (approximately $[Ni(AA)_2]_{20}$) in order to get a value of 2220 for M_w. This is certainly not a chemically appealing model of the solution.

It is perhaps not unreasonable to continue to believe that the trimeric structure preserves its integrity almost, if not entirely, quantitatively in solution, and to raise the question of whether the Brillouin light-scattering method is of proven trustworthiness as used in the present case.[7]

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