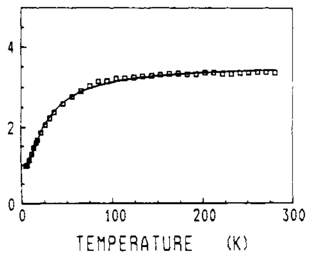
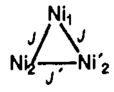


Figure 2. Temperature dependence of χ_mT. The molar magnetic susceptibility is referred to three nickel(II) ions. The solid line represents the best fit (see text).

spectra by the doublet at 2092 and 2106 cm^{-1}. In the far-IR spectrum, four new bands with respect to the free ligand molecule spectrum are found at 343, 318, 253, and 229 cm^{-1}. The bands below 300 cm^{-1} can be assigned to a large contribution of the Ni-N(thiocyanate) stretching modes.[15]

Magnetic Properties. The effective magnetic moments of $Ni_3(guanazole)_6(NCS)_6 \cdot 6H_2O$ are temperature dependent as shown by the χ_mT vs T plot of Figure 2.

In particular, χ_mT decreases with decreasing temperature, indicating a dominating antiferromagnetic coupling between the spins. The experimental data were fitted with the standard expression valid for trinuclear species.[16,17] The input parameters are the g values of the terminal and internal nickel(II) ions, respectively, and the coupling constants defined by



The best fit values are $J = 9.32$ (5) cm^{-1}, $J' = 3.4$ (1) cm^{-1}, $g_1 = 2.27$ (2), and $g_2 = 2.16$ (1). We use the spin Hamiltonian in the form $H = J\mathbf{S}_1 \cdot \mathbf{S}_2$. As is usual in trinuclear complexes, the value of J' can be determined with only limited accuracy.[18,19] If J' is fixed at zero, then J is calculated as 10.32 (3) cm^{-1}. Reasonable equivalent fits can be obtained also introducing small zero-field splitting of the ground triplet state. The value of J remains practically constant also in this case. The most reliable parameter that emerges from the analysis is the coupling between the internal and terminal ions, which is weak antiferromagnetic. The extent of the coupling, mediated by the triazole group, is fairly small, if we compare it with the value observed for instance in copper(II) triazolate complexes,[20] where values as large as 204–236 cm^{-1} have been observed. Beyond the difference due to the charged nature of the triazolates, which yield stronger interaction between the metal ions, the reason for this weak coupling must be that the triazolate planes are not parallel to those of the magnetic orbitals of the nickel ions. In fact in this geometry the overlap between the $x^2 - y^2$ and z^2 orbitals of terminal ions and the lone pair of the nitrogen atoms is smaller than in the copper complexes, where the $x^2 - y^2$ orbitals and the triazolates are coplanar. Similar arguments were used also for the mechanism of coupling through imidazolates.[21-23] The difference in the magnetic coupling between $Ni_3(detrH)_6(NCS)_6 \cdot 2H_2O$, which is weak ferromagnetic, and $Ni_3(guanazole)_6(NCS)_6 \cdot 6H_2O$, which is weak antiferromagnetic, must depend on the difference in structure between the two compounds. In fact, for the former two triazoles and one thiocyanate are bridging while for the latter three triazoles are bridging. Therefore, in a simple scheme, the observed difference can be attributed to the substitution of a thiocyanate bridge with one triazole. The weak ferromagnetic coupling in $Ni_3(detrH)_6(NCS)_6 \cdot 2H_2O$ therefore must be the sum of the contributions of two triazoles, which must be antiferromagnetic, and one thiocyanate, which must be ferromagnetic. This kind of coupling has already been observed in copper(II) dimers bridged by azide and isocyanate ions coordinating in an end-on fashion, and has been attributed to spin-polarization effects.[24-28] A similar mechanism might be operative in $Ni_3(detrH)_6(NCS)_6 \cdot 2H_2O$.

Conclusion. Despite the large sterical hindrance, three 3,5-diamino-1,2,4-triazole can be accommodated between two metal ions, yielding tri-μ-bridged structures.

The comparison of the magnetic properties of $Ni_3(guanazole)_6(NCS)_6 \cdot 6H_2O$ and $Ni_3(detrH)_6(NCS)_6 \cdot 2H_2O$ shows that the ferromagnetic coupling observed for the latter is essentially due to the bridging thiocyanate.

Acknowledgment. We are grateful to the Ministero della Pubblica Istruzione (MPI) of Italy for grants, to the Centro Interdipartimentale di Calcolo Automatico ed Informatica Applicata (CICAIA) of Modena University for computer facilities, and to the Centro Interdipartimentale Grandi Strumenti of Modena University for spectra recording and intensity data collection.

Registry No. $Ni_3(guanazole)_6(NCS)_6 \cdot 6H_2O$, 123774-92-5.

Supplementary Material Available: Tables SI–SV, listing a summary of the intensity data collection, anisotropic thermal parameters, positional and thermal parameters for hydrogen atoms, bond distances and angles involving hydrogen atoms and hydrogen bonding interactions, and selected least-squares planes (5 pages); a table of calculated and observed structure factors (3 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Reactions of a Perchlororhodium(I) Complex with Nitriles

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The perchlorato group in $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh, Ir) is so labile that it is readily replaced by various organic molecules (L) to produce cationic metal complexes $[M(L)(CO)(PPh_3)_2]ClO_4$,[1-5] which are catalytically active for the reactions of L.[2-5]

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Table I. Pseudo-First-Order Rate Constants (k_{obs}) for the Reaction $Rh(ClO_4)(CO)(PPh_3) + RCN \rightarrow [Rh(NCR)(CO)(PPh_3)_3]ClO_4$ in Chlorobenzene at 10 °C ([Rh] = 5.0×10^{-4} M)

RCN	[RCN], 10^{-3} M	k_{obs}, s^{-1}	k_{calcd}, s^{-1}
CH_3CN	5.02	1.91 ± 0.20	1.98
	7.50	2.68 ± 0.11	2.96
	10.10	3.87 ± 0.19	3.99
	12.40	4.77 ± 0.38	4.90
$CH_2{=}CHCH_2CN$	5.01	3.48 ± 0.11	2.82
	7.53	4.93 ± 0.52	4.14
	10.60	6.18 ± 0.38	5.98
	15.30	9.37 ± 0.93	8.63
$CH_2{=}CHCN$	5.05	28.80 ± 1.84	24.70
	7.47	42.20 ± 1.78	36.60
	10.40	55.10 ± 5.13	51.00
$CH_2{=}C(CH_3)CN$	6.28	33.80 ± 2.56	33.70
	7.55	35.60 ± 2.51	40.50
	10.40	46.00 ± 6.38	55.80
	15.30	82.20 ± 14.60	82.20
$CH_3CH{=}CHCN^a$	4.96	48.20 ± 3.74	49.40
	7.51	71.10 ± 5.80	74.80
	10.40	102.00 ± 8.13	104.00
	12.40	122.00 ± 26.50	124.00

[a] A mixture (cis/trans = ca. 3) of *cis*- and *trans*-$CH_3CH{=}CHCN$ was used.

Table II. Second-Order Rate Constants (k_2) and Activation Parameters for the Reaction $Rh(ClO_4)(CO)(PPh_3)_2 + RCN \rightarrow [Rh(NCR)(CO)(PPh_3)_2]ClO_4$ in Chlorobenzene

RCN	k_2, M^{-1} $s^{-1\,a}$	$\Delta H^\ddagger$, kcal/mol^b	$\Delta S^\ddagger$, cal/(deg mol)^b
CH_3CN	395 ± 32	11 ± 1.4	−8.7 ± 1.4
$CH_2{=}CHCH_2CN$	564 ± 51	11 ± 0.9	−8.4 ± 0.4
$CH_2{=}CHCN$	4900 ± 420	4.4 ± 0.3	−26 ± 1.0
$CH_2{=}C(CH_3)CN$	5370 ± 620	4.6 ± 0.2	−25 ± 0.8
$CH_3CH{=}CHCN^c$	10010 ± 1010	2.4 ± 0.2	−32 ± 0.8

[a] At 10 °C. [b] In the region 0–20 °C. [c] For a mixture (cis/trans = ca. 3) of *cis*- and *trans*-$CH_3CH{=}CHCN$.

No kinetic study has been carried out for the replacement of ClO_4^- in $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) with nitriles (eq 1) whereas equilibrium thermodynamic parameters have been obtained.[2,6] We now wish to report some kinetic data and suggest a mechanism for eq 1.

$$\underset{\mathbf{1}}{Rh(ClO_4)(CO)(PPh_3)_2} + RCN \rightarrow \underset{\mathbf{2}}{[Rh(NCR)(CO)(PPh_3)_2]ClO_4} \quad (1)$$

RCN = saturated and unsaturated nitriles

Experimental Section

Caution. Perchlorate salts of transition-metal complexes and perchlorato transition-metal complexes are potentially explosive.[7]

Materials. $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) was prepared by the literature method.[1] Nitriles were purchased from Fluka and Aldrich and used without further purification.

Kinetic Measurements. The reactions were followed with a Union Giken RA-401 stopped-flow spectrophotometer with RA-451 data processor by measuring the absorbances at the wavelengths (374–383 nm) of the absorption maximum for $[Rh(NCR)(CO)(PPh_3)_2]ClO_4$ (**2**)[8] under nitrogen in chlorobenzene at 0, 10, and 20 °C. The formation of cationic rhodium–nitrile complexes **2** was perfectly first order for at least 4 half-lives, and the pseudo-first-order rate constants (k_{obs}) were obtained from the logarithmic plots of absorbance differences versus reaction times, ln ($A_t - A_\infty$) vs time, where A_t and A_∞ are the absorbances of **2** at the absorption bands at time t and infinity, respectively. Least-squares fits were applied for the calculation of k_{obs}, activation parameters, and the corresponding errors. Those values in this report are the average ones determined in at least four or five runs.

Results and Discussion

It has been found that the reactions of **1** with nitriles (eq 1) are first order both in **1** and nitriles (see data in Table I), and the straight lines obtained from the plots of the pseudo-first-order rate constants (k_{obs}) versus concentration of nitriles (RCN) (data in Table I) go through the origin within the experimental error, which suggests the simple second-order rate law (eq 2) for the

$$-d[\mathbf{1}]/dt = k_{obs}[\mathbf{1}] = k_2[\mathbf{1}][RCN] \quad (2)$$

reaction (eq 1). Entropies of activation calculated from k_2 values in the region 0–20 °C are negative (Table II). These observations seem to agree with an associative mechanism through the formation of 18-electron five-coordinated intermediate $Rh(ClO_4)(NCR)(CO)(PPh_3)_2$ for the reaction (eq 1). The reaction (eq 1), however, is tentatively assigned an interchange mechanism in which there is a smooth interchange of the leaving perchlorate anion and the incoming nitriles, since there has been no definite evidence obtained thus far for the existence of the five-coordinated intermediate. Enthalpies of activation obtained (Table II) from k_2 values differ significantly from each other with respect to the incoming nitriles, which seems to suggest an associative mechanism (I_a) for eq 1.

Although no significant differences were observed in formation constants of eq 1 for various saturated[6] and unsaturated[2] nitriles, it is noticed in Table II that reactions are faster, enthalpies of activation are smaller, and entropies of activation are more negative for nitriles with conjugated olefinic group (conjugated nitriles) than for saturated and nonconjugated nitriles. It was reported that formation of π-complexes through the π-system of the olefinic group of unsaturated nitriles is favored by conjugation of the double bond with nitrile group.[9] The nitriles in $[Rh(NCR)(CO)(PPh_3)_2]ClO_4$, however, are known to coordinate to rhodium(I) through the nitrogen alone,[2] and coordination of conjugated nitriles through both the nitrogen and other functional group simultaneously is most unlikely for electronic and steric reasons.[10] Accordingly, the interaction between rhodium and the nitrogen atom of NCR is the most relevant subject to discuss the kinetic and activation parameters for eq 1. Lower activation enthalpies and more negative values of activation entropies observed for the conjugated nitriles than for nonconjugated nitriles may reveal more facile and stronger interaction between rhodium and nitrogen in transition state for conjugated nitriles than for nonconjugated nitriles. Contribution from the resonance form $Rh{=}N^+{=}C^-$ to the σ-bond between metal and nitrogen ($Rh{-}N{\equiv}C{-}$) was estimated to be only 5%, and the π-acceptor strength of nitrile is known to be far less important to the σ-bond strength.[11] Therefore, the resonance form above and π-acceptor character of the nitriles are not enough to explain the large differences in activation parameters obtained for conjugated and nonconjugated nitriles. It still remains obscure why conjugated nitriles interact more readily and significantly with rhodium than do nonconjugated nitriles.

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Registry No. $Rh(ClO_4)(CO)(PPh_3)_2$, 36593-52-9; CH_3CN, 75-05-8; $CH_2{=}CHCH_2CN$, 109-75-1; $CH_2{=}CHCN$, 107-13-1; $CH_2{=}C(CH_3)CN$, 126-98-7; $CH_3CH{=}CHCN$, 4786-20-3.

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